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Fluorine-containing Phosphorus Ylids

V.V.Tyuleneva, E.M.Rokhlin, and I.L.Knunyants

The methods of preparation and properties of phosphorus ylids containing fluorine atoms in the "alkylidene" component are considered with the exception of halogenomethylenephosphoranes and ylids which contain fluorine atoms only at an appreciable distance from the carbanionic centre.
The bibliography includes 87 references.

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I. INTRODUCTION

A review dealing with fluorine-containing halogenomethylenephosphoranes was published previously[1]. In contrast to these, other fluorine-containing phosphorus ylids are characterised by a wide variety of properties, are frequently entirely stable, and can be isolated and characterised. However, in certain instances, for example, when triphenylphosphine interacts with perfluoroisobutene, the intermediate formation of fluorine-containing phosphorus ylids is only postulated.

The Wittig reaction ("carbonyl-olefination"), which represents the main synthetic application of phosphorus ylids[2-7], has been less thoroughly investigated in relation to fluorine-containing phosphorus ylids. At the same time the chemistry of these compounds involves many interesting reactions, which are frequently unusual.

This review describes the methods of preparation and properties of phosphorus ylids containing fluorine atoms in the "alkylidine" component†. Fluorine-containing halogenomethylenephosphoranes have been excluded from consideration[1]. Phosphorus ylids containing fluorine atoms only at a considerable remove from the carbanionic centre, for example, $Ph_3P{=}CHC_6H_4CF_3$ [8] or $Ph_3P{=}CH(CH_2)_3CF_3$,[9] have also been disregarded, because in this case the influence of these atoms on the properties of the ylids is insignificant.

† The AIPS-FTOR (VINITI) automated information-seeking system was used in selecting the literature.

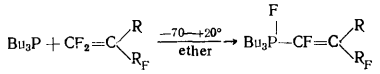
II. PREPARATION

The commonest methods of synthesising fluorine-containing phosphorus ylids are based on the reactions of tertiary phosphines with various fluorine-containing compounds—fluoro-olefins, fluoroalkyl halides, fluorothioketones, etc. Furthermore, it is possible to make use of methods involving the introduction of fluorine-containing groups into non-fluorinated phosphorus ylids.

1. Interaction of Tertiary Phosphines with Fluoro-olefins

The ability of fluoro-olefins to react with nucleophilic tertiary phosphines is due to the electrophilic properties of the former[10]#. The result then depends on the structure of the initial compounds and sometimes on the reaction conditions.

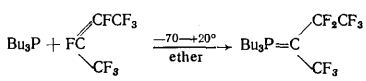
Substituted vinylfluorophosphoranes (I) have been obtained by the reaction of perfluoropropene and other terminal fluoro-olefins with tributylphosphine under mild conditions[11,12]§:



(I)

R	F	F	F	Ph	Ph
R_F	CF_3	n-C_3F_7	n-C_5F_{11}	CF_3	C_2F_5

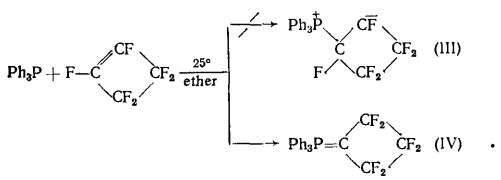
On treatment with tributylphosphine, perfluorobut-2-ene readily gives rise to the fluorine-containing phosphorus ylid (II):[11]



(II)

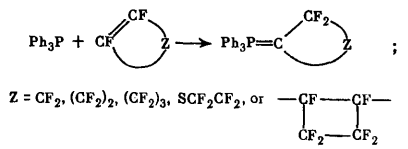
The structure of the ylid was demonstrated by NMR.

An anomalous reaction takes place when perfluorocyclobutene reacts with triphenylphosphine. Initially the betaine structure (III) was attributed to the reaction product[14], but later it was shown by X-ray diffraction[15] that perfluorocyclobutylidenetriphenylphosphorane (IV) is in fact formed¶:



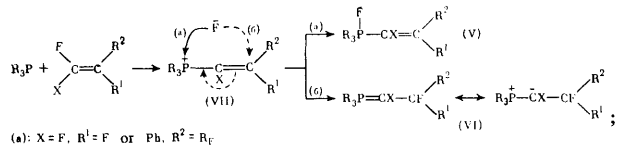
(III) (IV)

Other perfluorocycloalkylidenetriphenylphosphoranes have also been obtained by a similar procedure[16,19]:



Perfluorocyclohexene does not react with triphenylphosphine[16].

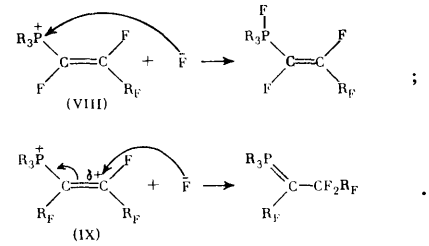
Thus, depending on the structure of the fluoro-olefin, either an alkenylfluorophosphorane (V) or a phosphorus ylid (VI) is formed on treatment with a tertiary phosphine. Evidently, the initial product must be an alkenylphosphonium fluoride (VII) in all cases. From the examples investigated (still very few), it has been suggested[11] that alkenylfluorophosphoranes are obtained only under conditions where the intermediate phosphonium cation contains a fluorine atom in the α-position†, while phosphorus ylids are produced when there is no α-fluorine atom:



(a): X = F, R^1 = F or Ph, R^2 = R_F

(b): X = CF_3, R^1 = F, R^2 = CF_3; XR^1 = $(CF_2)_2$, R^2 = F.

Probably in the latter case the crucial factor is not only the absence of a fluorine atom, but also the presence of the perfluoroalkyl group in the α-position. Perfluoroalkyl groups linked to the carbanionic centre impart stability to the phosphorus ylids (VI) (cf. Chambers[21]), while α-fluorine atoms destabilise the carbon ion (the Hine effect[22]). Another approach to the explanation of the results, associated with the consideration of the competitive influence of substituents on the polarisation of the C=C bond in the alkenylphosphonium cation, is also possible. In the cation (VIII) the partial positive charge on the β-carbon atom is insufficient to allow the attack on the latter by the F^- ion; therefore the positively charged phosphorus atom is attacked. In the cation (IX) the electron-accepting ability of both the perfluoroalkyl and the phosphonium group leads to an appreciable electrophilicity of the β-carbon atom, which promotes the formation of the phosphorus ylid:



(VIII) (IX)

It must be emphasised that the results obtained in the reaction of perfluorocyclobutene with trialkyl phosphite are apparently inconsistent with the proposed schemes. Under

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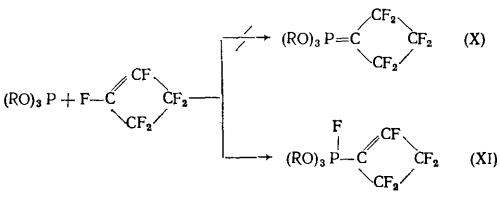
See Johnson[3] about the synthesis of phosphorus ylids by the interaction of tertiary phosphines with α,β-unsaturated carbonyl compounds.

§ The hydrolysis of these phosphoranes leads to α-hydroperfluoro-olefins[12]; thus a convenient method has been found for replacing the "vinyl" fluorine atom by a hydrogen atom. When perfluorobutadiene is treated with tertiary phosphines, relatively unstable cyclic phosphoranes are produced[13].

¶ Analogous ammonium[16-18] and arsonium[16] ylids have also been obtained. When perfluorocyclobutene reacts with tris-(dimethylamino)phosphine, only the products of the substitution of the fluorine atom by the dimethylamino-group are formed[16].

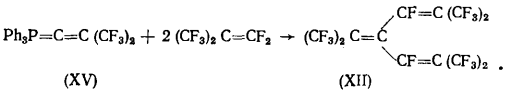
† There is evidence[20] that the phosphorus ylid $Ph_3P=CFCF_2CF_3$ rapidly isomerises to the fluorophosphorane $Ph_3PFCF=CFCF_3$.

these conditions, the product is the substituted vinylfluorophosphorane (XI) and not the phosphorus ylid (X):[23,24]#



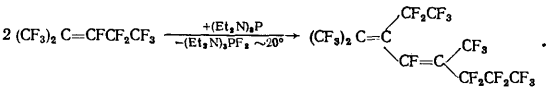
A particularly electrophilic fluoro-olefin—perfluoroisobutene—reacts with tertiary phosphines in an unusual manner. The reaction with triphenylphosphine[25] or with tributylphosphine[26] in acetonitrile§ led to the formation of a cross-conjugated perfluorotriene (XII). The diene (XIII) is formed together with this compound[26]. It has been suggested[25] that the reaction proceeds via a mechanism involving the intermediate formation of perfluoroisobutenylfluorophosphorane (XIV) and its defluorination product—the fluorine-containing cumulene ylid (XV). The addition of a second perfluoroisobutene molecule to the ylid (XV) led to the dienylfluorophosphorane (XVI), which split off triphenylphosphine and gave rise to the diene (XIII). On the other hand, the defluorination of the phosphorane (XVI) and subsequent addition of a third perfluoroisobutene molecule resulted in the formation of the trienylfluorophosphorane (XVII); the perfluorotriene (XII) was produced as a result of the elimination of triphenylphosphine.

The proposed mechanism of the defluorodimerisation and defluorotrimerisation of perfluoroisobutene has found some confirmation by the fact that the reaction of the known ylid (XV) with perfluoroisobutene also yielded the triene (XII):[26]

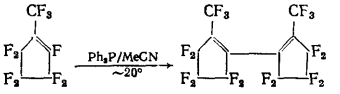


In contrast to perfluoroisobutene, perfluoropropene[25] and the ester of perfluoromethacrylic acid[28] merely dimerise on treatment with triphenylphosphine; analogous reactions on treatment with other bases had been described earlier[27,29,30]¶.

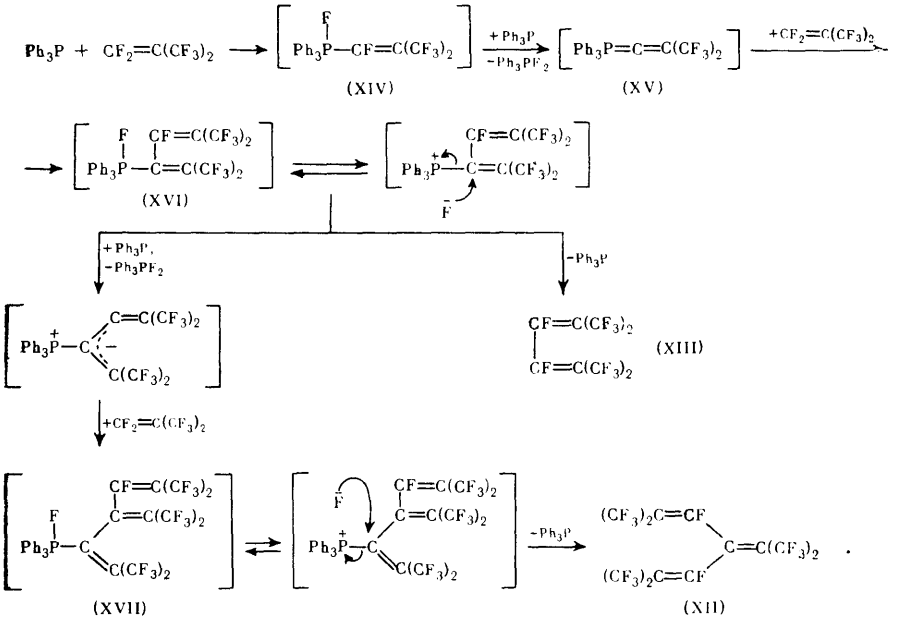
Perfluoropropene reacts vigorously with tris(dimethylamino)phosphine (the relevant paper gives no information about the products)[11]. The perfluoropropene dimer—perfluoro-2-methylpent-2-ene—undergoes defluorodimerisation on treatment with tris(diethylamino)phosphine[32]:



Perfluoro-1-methylcyclopentene reacts similarly with triphenylphosphine[32]:



Scheme



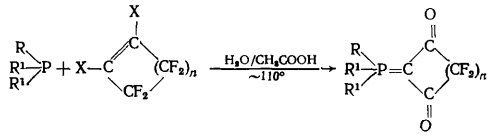
The decomposition of the adduct (XI) on heating leads to products of the substitution of the β-fluorine atom by an alkoxy-group[24] in addition to the products of the Arbuzov rearrangement[23].

§ The reaction in ether yielded the phosphoranes $(CF_3)_2C{=}CFPF_2Bu_2$ and $(CF_3)_2C{=}CBuPF_2Bu_2$, probably via the intermediate formation of the phosphorane $(CF_3)_2C{=}CFPFBu_3$.[26] When perfluoroisobutene was treated with trialkyl phosphites, the stable phosphoranes $(RO)_3PFCF{=}C(CF_3)_2$ were obtained; on heating they give rise to products of the Arbuzov rearrangement[23,27].

¶ Trialkyl phosphites react with perfluoropropene to give the products of the Arbuzov rearrangement[31], while the reactions with perfluoromethacrylic acid esters give rise to the fluorophosphoranes $(RO)_3PFCF{=}C(CF_3)COOR^1$, which decompose on heating into $ROPF_2$ and $(RO)_2C{=}C(CF_3)COOR^1$.[27]

The mechanism of these reactions is probably analogous to that of the conversion of perfluorisobutene into the diene (XIII).

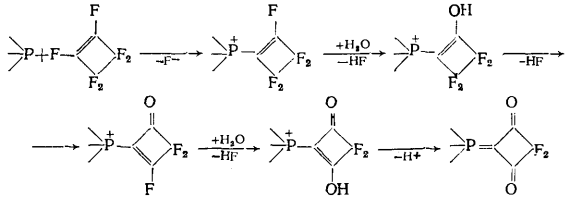
On treatment with tertiary phosphines in the presence of acetic acid and water, the cyclic diketo-ylids (XVIII) are formed from 1,2-dichloroperfluorocycloalkenes or perfluorocycloalkenes (C_4 and C_5):[14,33,34]



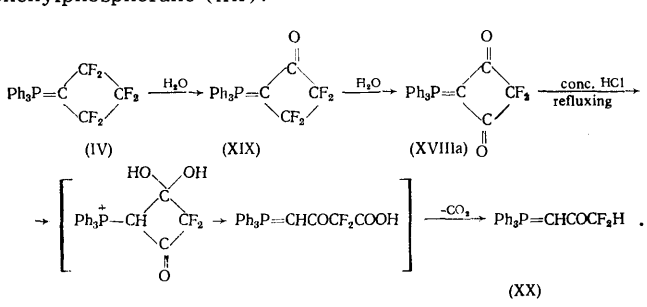
n	1	1	2	2	2	2
R	Ph	Ph	Ph	Ph	Bu	Bu
R^1	Ph	Ph	Ph	Ph	Ph	Bu
X	Cl	F	Cl	F	Cl	Cl

(XVIII): a—R=R^1=Ph, n=1; b—R=R^1=Ph, n=2; c—R=R^1=n-Bu, n=2; d—R=n-Bu, R^1=Ph, n=2.

A mechanism involving vinyl substitution on treatment with phosphine followed by the hydrolysis of the fluorine atoms has been proposed for this reaction[14], for example:



The hydrolysis of perfluorocyclobutylidenetriphenylphosphorane (IV) leads to the monoketo-ylid (XIX) [16] or the diketo-ylid (XVIIIa).[14,15]. Under more severe conditions, the diketo-ylid decomposes, forming difluoroacetylmethylenetriphenylphosphorane (XX):[34]

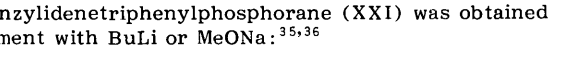


(IV) (XIX) (XVIIIa) (XX)

On refluxing with a tertiary phosphine in aqueous acetic acid solution, perhalogenocyclohexenes do not give rise to the corresponding diketo-ylids[14]. Triphenylphosphine oxide and 2-chloro-1-hydroperfluorocyclohexene are formed from 1,2-dichloroperfluorocyclohexene and Ph_3P under these conditions[34].

2. Interaction of Tertiary Phosphines with Other Organofluorine Compounds

Certain fluorine-containing phosphorus ylids can be obtained by the method most widely used for the synthesis of phosphorus ylids in general—by the dehydrohalogenation of phosphonium salts (the "salt method").[3] Thus alkylation of triphenylphosphine with pentafluorobenzyl bromide led to the corresponding phosphonium salt, from which pentafluorobenzylidenetriphenylphosphorane (XXI) was obtained on treatment with BuLi or MeONa:[35,36]

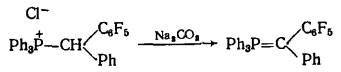


(XXI)

Triphenylphosphine was used as the dehydrobrominating agent in the reaction with α-bromopentafluoroacetophenone[37]:

(XXII); m.p. 134—137°.

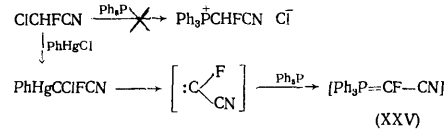
Pentafluorodiphenylmethyltriphenylphosponium chloride (XXIII) is converted into pentafluorodiphenylmethylenetriphenylphosphorane (XXIV) even on treatment with sodium carbonate[38]:



(XXIII) (XXIV); m.p. 206—209°.

According to patent data[39-42], the ylid $Ph_3P{=}CH(CH_2)_2CF_2$. .COOH has been obtained by treating the corresponding phosphonium salt with sodium hydride.

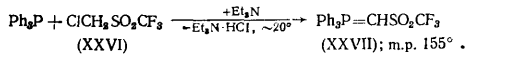
The "salt" method is frequently unsuitable for the synthesis of fluorine-containing phosphorus ylids. Thus, in contrast to pentafluorobenzyl bromide, decafluorodiphenylmethyl bromide[43] and the compounds $(CF_3)_2CHX$ [20,44] are incapable of alkylating triphenylphosphine. 2,2,2-Trifluoroethyl iodide reacts slowly with Ph_3P on irradiation, but trifluoroethyl idenetriphenylphosphorane $Ph_3P{=}CHCF_3$ cannot be obtained from the phosphonium salt formed[45]. The ester of chlorofluoroacetic acid[46] and its nitrile[47] also failed to give rise to quaternary salts on reaction with triphenylphosphine. However, the corresponding phosphorus ylid (XXV) can be obtained from the nitrile by a different method—via chlorocyanofluoromethyl(phenyl)mercury:[47,48]



(XXV)

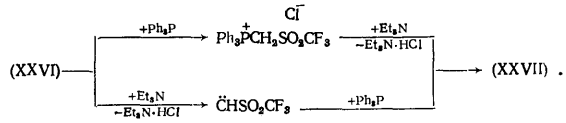
A carbene (cyanofluoromethylene) may be formed as an intermediate in this process†.

The stable trifluoromethanesulphonylmethylenetriphenylphosphorane (XXVII) has been obtained from chloromethyl trifluoromethyl sulphone (XXVI) and triphenylphosphine in the presence of triethylamine[50]:



(XXVI) (XXVII); m.p. 155°.

A phosphonium salt is probably formed initially and is then dehydrohalogenated by triethylamine, although the "carbene" mechanism is not ruled out:



Another mechanism has been proposed for the reaction of the sulphone (XXVI) with the chlorides of diphenyl- and diethyl-phosphinous acids. It has been suggested that this involves the initial substitution of the chlorine atom attached to the phosphorus atom with formation of tertiary phosphines (XXVIII), which rearrange to the more stable *P*-chlorosubstituted phosphorus ylids (XXIX),[50] probably as a result of

† The phosphorus ylid $(CF_3)_3F{=}CFCHF_2$ is formed when tris(trifluoromethyl)phosphine interacts with trifluoroethylidene generated from the silane $HCF_2CF_2SiF_3$ or from difluoromethylperfluorocyclopropane[49].

the nucleophilic attack by the phosphorus atom on the halogen, which has been rendered positive:

$$R_2PCl + ClCH_2SO_2CF_3 \xrightarrow[-Et_3N\cdot HCl]{+Et_3N} \left[R_2\overset{+}{P}-CHSO_2CF_3 \;\; Cl^-\right] \longrightarrow R_2P(Cl)=CHSO_2CF_3 ;$$

(XXVI) (XXVIII) (XXIX)

R = Et (XXIXa) or Ph.

The ylid (XXIXa) has also been obtained by the reaction of trifluoromethanesulphonylmethyldiethylphosphine (XXX) with carbon tetrachloride in the presence of triethylamine[51,52]:

$$Et_2PCH_2SO_2CF_3 \xrightarrow[ether,\ 0-20^\circ]{Et_3N} \left[Et_2P-\overset{-}{C}HSO_2CF_3 \leftrightarrow Et_2\overset{+}{P}=CHSO_2CF_3\right] \xrightarrow[-CCl_3^-]{+CCl_4} Et_2P(Cl)=CHSO_2CF_3$$

(XXX)

The chlorine atom in the phosphorus ylids (XXIX) is readily substituted by the diethylamino-group on treatment with Et_2NH.[50,51,53]

Sulphonylmethylphosphine (XXX) reacts with chlorodiethylphosphine in the presence of triethylamine to form an unusual phosphorus ylid (XXXI) containing the P–P bond[51,53]. The same phosphinophosphorus ylid is formed on heating sulphonylmethylphosphine in the absence of other reactants[51] and also from chlorodiethylphosphine and methyl trifluoromethyl sulphone[53]:

$$Et_2PCH_2SO_2CF_3 \xrightarrow[Et_3N]{Et_2PCl} Et_2P(Et_2P)=CHSO_2CF_3$$

(XXX) (XXXI); m.p. 51–53°;

$$2\ (XXX) \xrightarrow[\longleftarrow]{120^\circ/0.1\ mmHg} (XXXI) + CH_3SO_2CF_3 ;$$

$$2Et_2PCl + CH_3SO_2CF_3 \xrightarrow[ether]{Et_3N} (XXXI) ;$$

$$2Et_2PCl + M_2CHSO_2CF_3 \xrightarrow{THF} (XXXI) ;$$

M = Li or MgCl.

The structure of the *P*-substituted ylids (XXIX) and (XXXI) as well as related compounds has been confirmed by spectroscopic data. Thus the infrared spectra exhibit a characteristic bathochromic shift of the SO_2 absorption frequencies under the influence of the electron-donating "ylid" carbon atom[50,51]. The non-equivalence of the two dialkylphosphinyl groups is clearly manifested in the ^1H and ^{31}P NMR spectra of ylids of type (XXXI).[51]

The salts of phosphinodisulphone (XXXII) are alkylated with transfer of the reaction centre and the formation of the phosphorus ylids (XXXIII):

$$Ph_2P-\overset{-}{C}(SO_2CF_3)(SO_2Ph) \xrightarrow{RX} Ph(R)P(Ph)=C(SO_2CF_3)(SO_2Ph) ;$$

(XXXII) $H_2\overset{+}{N}Et_2$ (XXXIII); R = Me, m.p. 158°; R = Et, m.p. 174–176°.

The structure of ylids of type (XXXIII) has been inferred from their infrared spectra[51,54].

A promising method of synthesising fluorine-containing ylids apparently involves the interaction of tertiary phosphines with fluorine-containing thioketones#. Thus the unstable hexafluoroisopropylidenetriphenylphosphorane (XXXV) has been obtained from triphenylphosphine and thiohexafluoroacetone [in the form of the dimer (XXXIV)]:[20]

$$2Ph_3P + (CF_3)_2C\langle S\rangle C(CF_3)_2 \xrightarrow[-78^\circ]{ether} 2\,[Ph_3\overset{+}{P}-S-\overset{-}{C}(CF_3)_2] \rightarrow$$

(XXXIV)

$$\xrightarrow[-2Ph_3PS]{} 2\,[:C(CF_3)_2] \xrightarrow{+2Ph_3P} 2\,[Ph_3P=C(CF_3)_2] .$$

(XXXV)

The reaction mechanism has not been demonstrated. It may be that bis(trifluoromethyl)carbene is formed as an intermediate.

The phosphorus ylid (XXXV) has been used successfully *in situ* in the Wittig reaction (see below). The use of tributylphosphine or tris(dimethylamino)phosphine instead of triphenylphosphine in an analogous reaction leads to a decrease of the yield of olefins[20]. In an earlier study[60] of the interaction of the dimer (XXXIV) with tributylphosphine only Bu_3PF_2 was isolated.

It was not possible to obtain the ylid (XXXV) from triphenylphosphine and other sources of bis(trifluoromethyl)carbene. Triphenylphosphine does not react with bis(trifluoromethyl)diazirine even under severe conditions[61], while the reaction with bis(trifluoromethyl)diazomethane yields the iminophosphorane (XXXVI):[62]

$$Ph_3P \xrightarrow{+(CF_3)_2C(N=N)} \text{(XXXV)}$$

$$Ph_3P \xrightarrow{+(CF_3)_2\overset{-}{C}-\overset{+}{N}\equiv N} Ph_3P=N-N=C(CF_3)_2 .$$

(XXXVI)

The stable hexafluoroisopropylidenetrialkoxyphosphoranes have been obtained from the dimer (XXXIV) and trialkyl phosphites(XXXVII):[60,63]

$$4\,(RO)_3P + (CF_3)_2C\langle S\rangle C(CF_3)_2 \xrightarrow{-30^\circ} 2\,(RO)_3P=C(CF_3)_2 + 2\,(RO)_3PS$$

(XXXIV) (XXXVII)

R	Me (a)	Et	iso-Pr	n-$C_{12}H_{25}$
b.p.	61–62°/0.35 mmHg	74–75°/0.25 mmHg	75–76°/0.05 mmHg	– (decomp.)

The interaction of tertiary phosphines with hexafluoroacetone *N*-alkenylimines (XXXVIII) led to the formation of substituted phosphorus ylids (XXXIX), probably as a consequence of the prototropic rearrangement of the intermediate betaines (XL):[64,65]

$$R^1_3P + R^2CH=CH-N=C(CF_3)_2 \xrightarrow[\text{hexane or benzene}]{0-20^\circ} [R^1_3\overset{+}{P}-CH(R^2)-CH=N-\overset{-}{C}(CF_3)_2] \xrightarrow{O}$$

(XL)

$$\longrightarrow R^1_3P(R^2)=C-CH=N-CH(CF_3)_2 .$$

(XXXIX)

R^1	Ph	iso-Pr	iso-Pr
R^2	Ph	Ph	iso-Pr
M.p.	138°	84°	– (oil)

When trialkyl phosphites are used instead of phosphines, the relatively unstable ylids (XLI) are formed and readily rearrange (see below):[64,65]

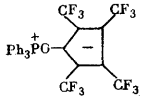
$$(R^1O)_3P + R^2CH=CHN=C(CF_3)_2 \xrightarrow{\sim 20^\circ} (R^1O)_3P(R^2)-C-CH=NCH(CF_3)_2$$

(XXXVIII)

(XLI); b.p. 93–96°/0.01 mmHg§;

R^1 = Me, Et, or iso-Pr; R^2 = Ph, or iso-Pr

The interaction of tertiary phosphines with perfluoroketones and perfluoroaldehydes has been described[55–58]. The betaine



has been obtained from perfluorotetramethylcyclopentadienone and triphenylphosphine[59].

§ The boiling point of compound (XLI) with $R^1=R^2$=iso-Pr is indicated.

3. Interaction of Phosphorus Ylids with Fluorine-containing Compounds

Phosphorus ylids are very readily acylated[3], such reactions including also those occurring on treatment with derivatives of fluorine-containing carboxylic acids. Thus the stable trifluoroacetylmethylenetriphenylphosphorane (XLII) has been obtained from methylenetriphenylphosphorane and ethyl trifluoroacetate[66]. When the initial ylid is generated with the aid of butyl-lithium, butyldiphenylphosphorane (XLIII) is formed in addition to triphenylphosphorane (XLII); it has been shown that the phenyl group in the ylid (XLII) is substituted by the butyl group on treatment with n-BuLi:[66]

$$Ph_3P{=}CH_2 \xrightarrow[-70\to+25^\circ]{CF_3COOEt} Ph_3P{=}CHCOCF_3 \xrightarrow[25^\circ]{n\text{-}BuLi} \underset{\text{n-Bu}}{Ph_2P{=}CHCOCF_3}$$

(XLII) m.p. 233°; (XLIII); m.p. 138°.

The chlorides of perfluorocarboxylic acids can acylate also inactive phosphorus ylids. Thus perfluoroacylphosphorus ylids have been obtained from methoxycarbonylmethylenetriphenylphosphorane and the chloride of trifluoroacetic or perfluorobutyric acid (XLIV):[67]

$$Ph_3P{=}CHCOOMe \xrightarrow{R_FCOCl} \underset{\underset{COR_F}{|}}{Ph_3P{=}CCOOMe}\ ;$$

(XLIV)

$R_F = CF_3$, or $n\text{-}C_3F_7$.

Cyanomethylene- and ethoxycarbonylmethylene-triphenylphosphoranes react with the dichloride of perfluoroglutaric acid to give stable bisylids (XLV):[45]¶

$$4Ph_3P{=}CHR + ClCO(CF_2)_3COCl \xrightarrow[\text{benzene}]{25^\circ} \underset{\text{(XLV)}}{Ph_3P{=}CRCO(CF_2)_3COCR{=}PPh_3} + 2Ph_3\overset{+}{P}CH_2R\ Cl^-\ ;$$

m.p. 248–260° (R=CN), 194–195° (R=COOEt).

The initial phosphorus ylid is taken in excess in order to bind the HCl evolved.

The acylation of benzylidene- and pentafluorobenzylidenetriphenylphosphoranes by pentafluorobenzoyl chloride led to stable fluorine-containing phosphorus ylids (XLVI)[35]:

$$Ph_3P{=}CHR + C_6F_5COCl \xrightarrow[\text{benzene}]{15^\circ} \underset{\text{(XLVI)}}{Ph_3P{=}CRCOC_6F_5}\ ;$$

m.p. 244–247° (R=Ph), 245–246° ($R=C_6F_5$).

Active phosphorus ylids are capable of reacting with hexafluorobenzene[38] and with 2-phenylperfluoropropene[68] to form pentafluorophenylylids [(XXI) or (XXIV)] and the phenylperfluoropropenylylid (XLVII):

$$Ph_3P{=}CHR + C_6F_6 \xrightarrow[\text{ether}]{\sim 20^\circ} [Ph_3\overset{+}{P}CHRC_6F_5\ \bar{F}] \xrightarrow[-Ph_3\overset{+}{P}CH_2R\ \bar{F}]{+Ph_3P{=}CHR} Ph_3P{=}CRC_6F_5\ ;$$

R=H (XXI), or Ph (XXIV);

$$2Ph_3P{=}CHMe + CF_2{=}CPhCF_3 \xrightarrow{\sim 20^\circ} \left[Ph_3P{=}\underset{\underset{Me}{|}}{C}{-}CF{=}C\begin{matrix}Ph\\CF_3\end{matrix}\right] + Ph_3\overset{+}{P}CH_2Me\ \bar{F}\ .$$

(XLVII)

Under the reaction conditions, the ylid (XLVII) splits off an F^- anion and is converted into the allenylphosphonium salt (XLVIII), whose hydrolysis gives rise to the allene (XLIX) as well as its isomerisation [compound (L)] and dehydrofluorination [compound (LI)] products[68]:

$$(XLVII) \rightarrow \left[Ph_3\overset{+}{P}{-}\underset{\underset{Me}{|}}{C}{=}C{=}C\begin{matrix}Ph\\CF_3\end{matrix}\ \bar{F}\right] \xrightarrow{H_2O} MeCH{=}C{=}C\begin{matrix}Ph\\CF_3\end{matrix} +$$

(XLVIII) (XLIX)

$$+ MeC{\equiv}C{-}\underset{\underset{Ph}{|}}{CH}{-}CF_3 + MeC{\equiv}C{-}\underset{\underset{Ph}{|}}{C}{=}CF_2\ .$$

(L) (LI)

The chemistry of cumulene phosphorus ylids has appreciably developed recently[5]. In particular, hexaphenylcarbodiphosphorane (LII) and the "ylidoketen" (LIII) are of interest.

The ylid (LII) reacts with hexafluoroacetone to form the extremely stable "ylido-oxaphosphetan" (LIV);[69–73] an analogous result was obtained using dodecafluorotetramethylethylenedioxytriphenylphosphorane (LV) instead of hexafluoroacetone[72]:

$$Ph_3P{=}C{=}PPh_3 + (CF_3)_2CO \xrightarrow[\text{diglyme}]{40\text{–}50^\circ} \underset{\text{(LII)}}{\quad} \xrightarrow{} Ph_3P{=}\underset{\underset{(CF_3)_2C{-}O}{|}}{C}{-}PPh_3$$

(LII) + Ph_3P (LV) $\xrightarrow[\text{diglyme}]{65\text{–}75^\circ}$ (LIV), m.p. 157–158°

Thus a stable cyclic adduct of a phosphorus ylid with a ketone—the intermediate of the Wittig reaction—was in this instance isolated and characterised for the first time. The structure of the adduct (LIV) was demonstrated by X-ray diffraction[74]. Its stability can be accounted for by the strengthening of the C–O bond by the influence of the trifluoromethyl groups and the high electron density at the carbon atom linked to the phosphorus atom, which apparently prevents the dissociation of the C–P bond[72].

However, when the adduct (LIV) is heated above 110 °C, the second stage of the Wittig reaction nevertheless takes place—the adduct splits into the phosphine oxide and hexafluoroisobutenylidenetriphenylphosphorane (XV):[69–73]

$$(LIV) \xrightarrow[5\text{–}10\ min]{120\text{–}125^\circ} Ph_3P{=}C{=}C(CF_3)_2 + Ph_3PO\ .$$

The cumulene ylid (XV) cannot be fully separated from triphenylphosphine oxide.

When the adduct (LIV) reacts with various acids, phosphonium salts are formed and these can also be regarded as substituted phosphorus ylids[70–73] (see Section III, 3 below).

The "ylidoketen" (LIII) reacts with hexafluoroacetone and p-chloro-α,α,α-trifluoroacetophenone to form diketo-ylids (LVI), probably as a result of the cycloaddition of the initial ylid to the alkylideneketen (LVII), formed by the Wittig reaction[75]:

$$Ph_3P{=}C{=}C{=}O + \underset{R}{\overset{CF_3}{C{=}O}} \xrightarrow{-Ph_3PO} \left[\underset{R}{\overset{CF_3}{C{=}C{=}C{=}O}}\right] \xrightarrow{+(LIII)}$$

(LIII) (LVII)

$$\longrightarrow Ph_3P{=}\underset{\underset{\underset{O}{\|}}{C}}{\overset{\overset{O}{\|}}{C}}{=}\underset{\underset{R}{|}}{\overset{CF_3}{C}}\ ;$$

(LVI)

R=n-ClC_6H_4 (m.p. 246–247°), or CF_3.

¶ The ylid $Ph_3P{=}CFCN$ (XXV) cannot be obtained from cyanomethylenetriphenylphosphorane by fluorination with $FClO_3$.[43]

4. The Preparation of Wittig–Horner Reagents

The α-phosphonate carbanions, formed when the esters of alkylphosphinic acids are treated with bases, are analogues of phosphorus ylids:

$$(RO)_2PCHXY \xrightarrow[-BH]{+B^-} (RO)_2\bar{P}-CXY \leftrightarrow (RO)_2P=CXY \ .$$

These carbanions are widely used for the "olefination" of carbonyl compounds (the Wittig–Horner reaction).

The diethyl ester of α-fluoroethoxycarbonylmethylphosphonic acid was obtained by the Arbuzov reaction from the ester of bromofluoroacetic acid and triethyl phosphite and was converted on treatment with sodium or sodium hydride into the stable fluorine-containing anion (LVIII):[76–78]

$$(EtO)_3P + BrCHFCOOEt \xrightarrow[-EtBr]{145^\circ} (EtO)_2PCHFCOOEt$$

$$\xrightarrow[ether,\ \sim 0^\circ]{Na \text{ or } NaH} (EtO)_2\bar{P}CFCOOEt \ .$$

(LVIII)

The phosphonate carbanion obtained was used to synthesise the esters of unsaturated α-fluorine-substituted carboxylic acids (see Section III, 2 below).

The phenyl-substituted phosphonate carbanion (LIX), obtained from the ester of α-hydroxybenzylphosphonic acid, has been used to synthesise α-fluorostilbene (see Section III, 2 below):[79]

$$(EtO)_2PCHPh \xrightarrow{Et_2NCF_2CHFCl} (EtO)_2PCHPh \xrightarrow{-H^+} (EtO)_2\bar{P}CFPh \ .$$

(LIX)

III. PROPERTIES

The properties of fluorine-containing phosphorus ylids depend to a large extent on the nature of the substituents at the phosphorus atom and at the carbanionic centre.

1. Stability. Physical and Physicochemical Properties

The phosphorus ylids containing acyl or sulphonyl groups capable of delocalising the negative charge are distinguished by a special stability[4,7]†. Polyfluoroacyl- and polyfluoroalkanesulphonyl-methylenephosphoranes should be still more stable owing to the electron-withdrawing effect of the polyfluoroalkyl groups. Special studies in this field have not been made. However, there are data indicating a special stability of fluorine-containing phosphorus ylids such as trifluoroacetylmethylenetriphenylphosphorane (XLII),[66] pentafluorobenzoylmethylenetriphenylphosphorane (XXII),[37] and trifluoromethanesulphonylmethylenediethylchlorophosphorane (XXIXa).[51] Pentafluorodiphenylmethylenetriphenylphosphorane (XXIV) is still more stable than its non-fluorinated analogue[38].

† In general the phosphorus ylids $R_3^3P=CR^1R^2$ can be divided into three groups: the reactive ylids (R^1, R^2 = H or alkyl), the "moderate" ylids (R^1 = 1-alkenyl, 1-alkynyl, aryl, or halogeno-group; R^2 = ditto, H, or alkyl), and the stable ylids (R^1 = COR, COOR, CN, or SO_2R; R^2 = any group)[7].

Like the alkoxycarbonyl groups, the trifluoromethyl groups can stabilise carbanions[21]. It was therefore to be expected that ylids of the type $R_3P=C(CF_3)_2$ are extremely stable. However, it was found that hexafluoroisopropylidenetriphenylphosphorane (XXXV) is unstable and can be used in the Wittig reaction *in situ*[20]. It may be that the instability of such compounds can be accounted for by their stability to eliminate fluoride ion from the β-position. Analogous β-elimination in the case of the alkenylylid (XLVII) leads to the allenylphosphonium salt (XLVIII)[68] (see Section II, 3 above). However, ylids such as hexafluoroisopropylidenetrialkoxyphosphoranes (XXXVII)[60] and perfluorocyclobutylidenetriphenylphosphorane (IV)[17] proved to be extremely stable.

The stable fluorine-containing phosphorus ylids isolated are usually high melting crystalline substances. However, under the usual conditions some of them are liquids [for example, $Et_2PCl=CHSO_2CF_3$ (XXXIXa)[50,52] or $(R^1O)_3P=CR^2CH=NCH(CF_3)_2$ (XLI)[64,65]].

Table 1. The chemical shifts in the ^{31}P NMR spectra of fluorine-containing phosphorus ylids.

Ylid	Chemical shift, p.p.m.	References	Ylid	Chemical shift, p.p.m.	References
(II)	−23.7*	[11]	(XVIIIc)	−21.7**	[14]
(IV)	−5.6**	[14]	(XVIIId)	−12.8**	[14]
(XV)	−4.1*	[72]	(LIV)	−7.3 and +54.0*	[71, 72]
(XVIIIa)	−3.0*, −4.1**	[75, 14]	(LVI)	−1.9*	[75]
(XVIIIb)	−10.2**	[14]	(LXII)	−21 ÷ −22*	[72]

*Relative to the external standard—85% H_3PO_4.
**Relative to the internal standard—$(EtO)_3PO$.

The spectra of certain fluorine-containing phosphorus ylids have been investigated: infrared[14,34,45,50–52,54,64–66,75], ^1H NMR,[14,34,51,52,65,66,70–72] ^{19}F NMR,[11,14,17,34,38,50,60,70–73,75] ^{31}P NMR,[11,14,51,65,70–72,75] and mass spectra[75]. The structure of the ylids (IV) and (LIV) was confirmed by X-ray diffraction[15,72,74].

Table 2. The spin–spin coupling constants between ^{19}F and ^{31}P nuclei in fluorine-containing phosphorus ylids.

Ylid	*m**	*J*, Hz	Refs.	Ylid	*m**	*J*, Hz	Refs.
(XV)	4	3.5	[72]	(XXXVIIa)	3	13	[60]
(XVIIIa)	4	20.5	[34]	(LIV)	4	0.8	[72]
(XVIIIb)	4	1.1	[34]	(LVI)**	6	1.1	[75]

*Here *m* is the number of bonds separating the ^{19}F and ^{31}P nuclei.
**R = CF_3.

In the ^{31}P NMR spectra of fluorine-containing phosphorus ylids with three phenyl groups at the phosphorus atom the chemical shift due to the "ylid" phosphorus nucleus is in the range from −2 to −10 p.p.m. (Table 1). The replacement of the phenyl group by the n-butyl group leads to a downfield displacement of the ^{31}P NMR signal. Spin–spin interaction between the ^{19}F and ^{31}P nuclei, even those fairly remote from one another, is frequently observed in the ^{19}F NMR spectra (Table 2).

2. The Wittig Reaction

In contrast to halogenomethylenephosphoranes[1], the behaviour of other fluorine-containing phosphorus ylids in the Wittig reaction has still been inadequately investigated. As a rule these ylids exhibit a moderate or even a low reactivity in relation to carbonyl compounds. However, in certain cases it is possible to obtain fluorine-containing unsaturated compounds.

Hexafluoroisopropylidenetriphenylphosphorane (XXXV) reacts *in situ* under mild conditions with various aliphatic, aromatic, and heterocyclic aldehydes to form the corresponding olefins[20]#:

$$\underset{\text{(XXXV)}}{[Ph_3P{=}C(CF_3)_2]} + RCHO \xrightarrow[\text{ether}]{-78\div+20^\circ} \underset{\text{(yield = 26–62\%)}}{RCH{=}C(CF_3)_2} + Ph_3PO;$$

R=Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, $O_2NC_6H_4$, C_6F_5, PhMeCH, n-C_6H_{13}, PhCH=CH, 2-furfuryl, 2-pyridyl, or *m*-$CF_3C_6H_4$.

The reaction of the ylid (XXXV) with ketones cannot be achieved—owing to its low reactivity, there is sufficient time for its decomposition[20].

The cumulene ylid (XV) readily reacts with both aldehydes and ketones, but this leads to the formation of complex mixtures of unidentified substances[73]. The cumulated triene (LX) was isolated in the reaction with diphenylketen[72]:

$$\underset{\text{(XV)}}{Ph_3P{=}C{=}C(CF_3)_2} + Ph_2C{=}C{=}O \rightarrow \underset{\text{(LX)}}{Ph_2C{=}C{=}C{=}C(CF_3)_2} + Ph_3PO.$$

Pentafluorobenzylidenetriphenylphosphorane (XXI) reacts with pentafluorobenzaldehyde[36], *p*-chloro and *p*-nitro-benzaldehydes[38], and *t*-butyl- and trimethylsilyl-propiolaldehydes[80] to form the corresponding olefins:

$$\underset{\text{(XXI)}}{Ph_3P{=}CHC_6F_5} + RCHO \rightarrow RCH{=}CHC_6F_5;$$

R=C_6F_5, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$, $Me_3CC{\equiv}C$, or $Me_3SiC{\equiv}C$.

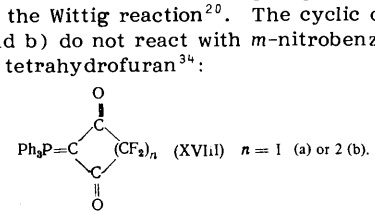
The *trans*-olefins are then usually formed preferentially.

trans-Decafluorochalcone (LXI) has been obtained by the reaction of pentafluorobenzoylmethylenetriphenylphosphorane (XXII) with pentafluorobenzaldehyde[37]:

$$\underset{\text{(XXII)}}{Ph_3P{=}CHCOC_6F_5} + C_6F_5CHO \rightarrow \underset{\text{(LXI)}}{C_6F_5CH{=}CHCOC_6F_5}.$$

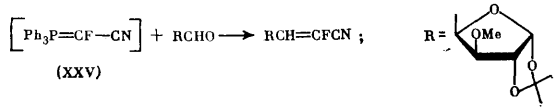
According to patent data[39–42], the phosphorus ylid $Ph_3P{=}CH(CH_2)_2CF_2COOH$ is used to synthesise fluorine-containing analogues of prostaglandin.

Perfluorocyclobutylidenetriphenylphosphorane (IV) does not undergo the Wittig reaction[20]. The cyclic diketoylids (XVIII, a and b) do not react with *m*-nitrobenzaldehyde on refluxing in tetrahydrofuran[34]:



(XVIII) $n = 1$ (a) or 2 (b).

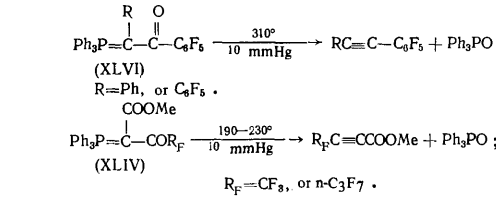
Cyanofluoromethylenetriphenylphosphorane (XXV) reacts with aldehydosugars to form the products of the Wittig reaction[47,48]:



(XXV)

It has been claimed[20] that the trimethoxy-ylid $(MeO)_3P{=}C(CF_3)_2$ (XXXVIIa) does not react either with benzaldehyde or with trifluoroacetophenone.

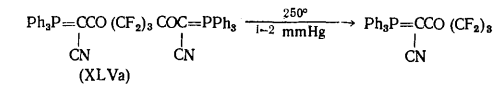
Like the usual acylmethylenephosphoranes, their fluorine-containing analogues—pentafluorobenzoylylids (XLVI) [35] and also trifluoroacetyl- and perfluorobutyryl-ylids (XLIV) [67]—are capable of undergoing the intramolecular Wittig reaction to form the corresponding acetylenes:



(XLVI) R=Ph, or C_6F_5.

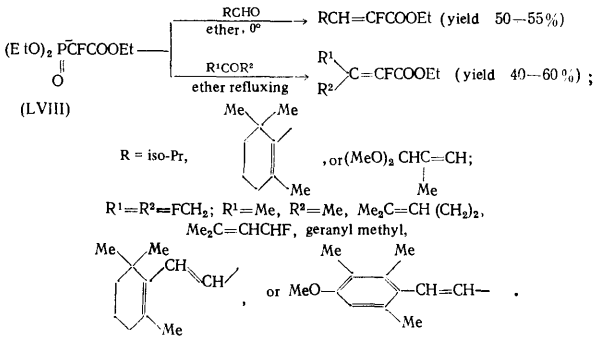
(XLIV) R_F=CF_3, or n-C_3F_7.

The diacetylenes $RC{\equiv}C(CF_2)_3C{\equiv}CR$ could not be obtained from the bisylids $Ph_3P{=}CRCO(CF_2)_3COCR{=}PPh_3$ (XLV, R=CN or COOEt); in the case of the dinitrile (XLVa) an ylid containing the C≡C triple bond was isolated[45]:



(XLVa)

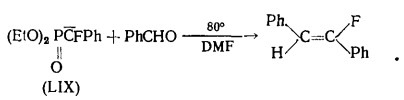
The Wittig–Horner reaction has also been used to synthesise fluorine-containing unsaturated compounds. The reaction of the stable α-phosphonatecarbanion (LVIII) with aldehydes and ketones yielded various unsaturated fluorine-containing esters[76–78]:



(LVIII)

In the reaction of the anion (LVIII) with ketones the yields of unsaturated compounds are lower than in the case of the analogous non-fluorinated anions. The reactions with asymmetric ketones give rise to mixtures of the *cis*- and *trans*-isomers, but the reaction with aldehydes is stereospecific—only the *cis*-isomers are obtained[76].

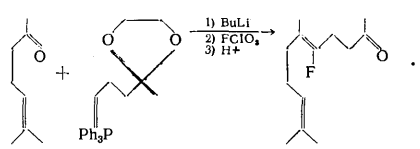
Trans-α-fluorostilbene has been obtained in 40% yield from the phenyl-substituted anion (LIX) and benzaldehyde[79]:



(LIX)

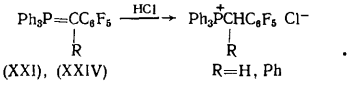
Fluorine-containing analogues of prostaglandin have been obtained with the aid of the Wittig–Horner reaction[81].

The SCOOPY (α-Substitution plus Carbonyl Olefination via β-Oxido Phosphorus Ylids) reaction is also used to synthesise fluorine-containing unsaturated compounds[7,82–85] (cf. Tyuleneva et al.[1]), for example:



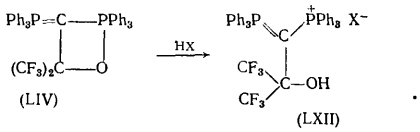
3. Other Reactions

Phosphorus ylids usually combine very readily with acids to form phosphonium salts[3]. Fluorine containing phosphorus ylids behave similarly. Thus the reaction of pentafluorophenylylids (XXI) and (XXIV) with dry HCl yielded phosphonium chlorides[38]:



(XXI), (XXIV) R=H, Ph

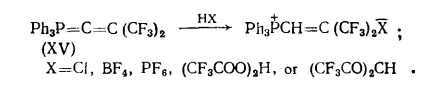
Analogous reactions with the cyclic ylid (LIV) lead to the dissociation of the P–O bond and the formation of the salts (LXII):[73]



(LIV) (LXII)

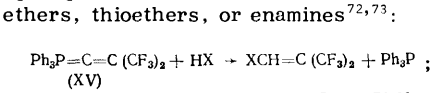
The salts (LXII) with X = Cl,[71] Br,[70] BF_4,[70,72] PF_6,[70–72] BPh_4,[70] or CF_3COO [72] have been obtained in this way.

Alkenylphosphonium salts have been synthesised from hexafluoroisobutenylidenetriphenylphosphorane (XV):[72]



(XV) X=Cl, BF_4, PF_6, $(CF_3COO)_2H$, or $(CF_3CO)_2CH$.

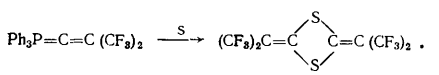
When the ylid (XV) is treated with alcohols, phenols, amines, or mercaptans the C–P bond is split with elimination of a tertiary phosphine and the formation of the corresponding alkenyl ethers, thioethers, or enamines[72,73]:



(XV) X=3, 4, 5-$Me_3C_6H_2O$, EtO, EtS, C_6Cl_5, or Ph_2N .

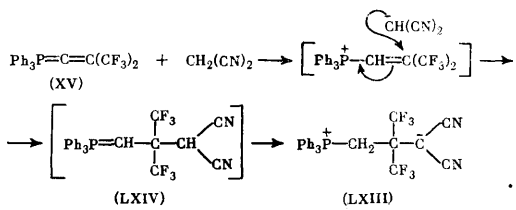
The reaction with *O*-deuteromethanol produced the deuterated ether $MeOCD{=}C(CF_3)_2$.[72]

The dimer of bis(trifluoromethyl)thioketen has been obtained from the ylid (XV) on treatment with sulphur:



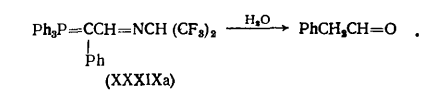
(XV)

Yet another reaction pathway is observed on treatment with malonodinitrile: this results in the formation of the betaine (LXIII), probably as a result of the prototropic isomerisation of the ylid (LXIV):[72]



(XV) (LXIV) (LXIII)

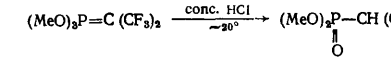
Hydrolysis of the phosphorus ylid (XXXIXa) leads to the splitting of the C=P and C=N bonds[65]:



(XXXIXa)

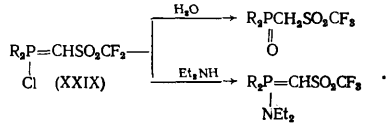
When perfluorocyclobutylidenetriphenylphosphorane (IV) is hydrolysed under mild conditions, the β-fluorine atoms are hydrolysed[14–16], whereas under severe conditions the ring is ruptured[34] (see Section II, 1 above). The diketo-ylid (XVIIIb) does not change on being refluxed with 50% sulphuric acid[34].

Hydrolysis of the trimethoxyphosphorus ylid (XXXVIIa) leads to a phosphonate ester[60]:



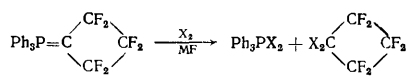
(XXXVIIa)

P-Chloro-ylids (XXIX) are converted on hydrolysis into phosphine oxides[50], while on treatment with diethylamine they give rise to phosphorus ylids containing the diethylamino-group at the phosphorus atom[50,51,53]:

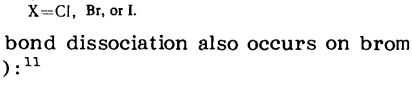


(XXIX)

The ylid (XXXVIIa) is readily brominated[60]:

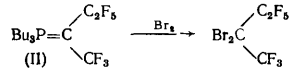


The diketo-ylids (XVIII, a and b) are not brominated and are not oxidised by permanganate[34]§. In the presence of metal fluorides, the more reactive ylid (IV) is halogenated with dissociation of the C=P bond[16]:



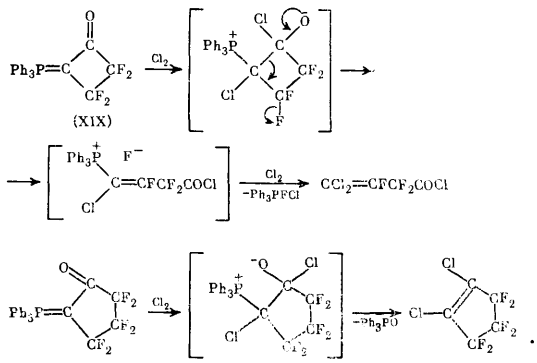
(IV) X=Cl, Br, or I.

A similar bond dissociation also occurs on bromination of the ylid (II):[11]



(II)

When the four-membered cyclic monoketo-ylid (XIX) is chlorinated, the ring is ruptured with formation of perhalogenovinylacetyl chloride; the five-membered analogue gives rise to dichloropentafluorocyclopentene[16]:



(XIX)

Stable cyclic diketoylids (XVIII, a and b) cannot be alkylated with methyl iodide on refluxing in acetone[34]. The ylid (LIV), containing the oxaphosphetan ring, also does not react with methyl iodide[71,72].

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§ On oxidation with CrO_3 in acetic acid, the ylid (XVIIIb) gives rise to perfluorosuccinic acid[34].

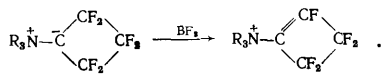
Pentafluorobenzylidenetriphenylphosphorane (XXI) is acylated at the "ylid" carbon atom[35] (see Section II, 3 above).

On treatment with metal salts, perfluorocyclobutylidenetriphenylphosphorane (IV) is converted into polyfluorocyclobutenylphosphonium salts[16]:

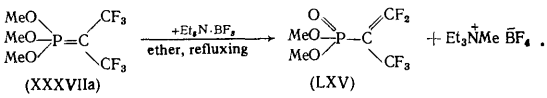


(IV)

The ylid structure is similarly converted into the cycloalkenylammonium structure on treatment of trialkylammonium perfluorocyclobutylids with boron trifluoride etherate[17]:

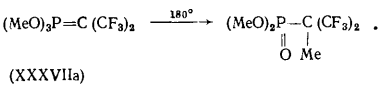


An analogous reaction is apparently possible also for the corresponding phosphorus ylids and the reverse reaction, involving the conversion of cycloalkenylphosphonium tetrafluoroborate into a phosphorus ylid—takes place on treatment with KF (cf. Burton and Shinya[11]). Treatment of the trimethoxyphosphorane (XXXVIIa) with the adduct of triethylamine and boron trifluoride leads to the simultaneous elimination of the alkyl group and the fluorine atom with formation of the phosphorus analogue of perfluoromethacrylic acid ester (LXV):[86]



(XXXVIIa) (LXV)

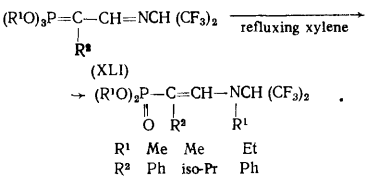
Certain phosphorus ylids containing alkoxy-groups at the phosphorus atom are capable of rearranging with transfer of the alkyl group from the oxygen atom to a carbon or nitrogen atom. Thus hexafluoroisopropylidenetrimethoxyphosphorane (XXXVIIa) is converted into the ester of hexafluoro-t-butylphosphonic acid on heating to 180 °C:[60]



(XXXVIIa)

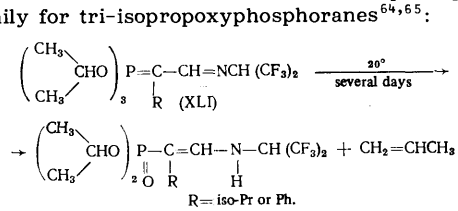
In the presence of SbF_5, the reaction temperature is reduced to 140 °C.[87]

The phosphorus ylids (XLI) are converted slowly at room temperature and rapidly on heating into substituted phosphonate esters containing an alkyl group at the nitrogen atom[64,65]:



R^1	Me	Me	Et
R^2	Ph	iso-Pr	Ph

Apart from a rearrangement, when the ylids (XLI) are heated, the elimination of the alkyl group R^1 in the form of an olefin is observed. Such a reaction takes place particularly readily for tri-isopropoxyphosphoranes[64,65]:



R= iso-Pr or Ph.

Thus fluorine-containing phosphorus ylids exhibit a varied reactivity. Further investigation of the chemistry of these interesting compounds is necessary.

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The Chemistry of Radon

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We shall review the discovery of this element, studies of its chemical nature, and modern ideas on its chemical and physical properties. Possible chemical and nuclear-chemical methods of synthesising new radon compounds and of determining their properties and their identity will be discussed, using information published up to May 1980. 121 references.

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I. INTRODUCTION

Only 20 years have passed since Bartlett[1] prepared the first compound of xenon. In this relatively short time many compounds of the elements of Group O of the Periodic Table have been synthesised and studied in detail. The large volume of work in this new branch of chemistry has already been reviewed several times[2-10], and the most recent work is discussed in a comprehensive review[11]. However, most of this work is aimed at the chemistry of xenon and krypton, and the chemistry of radon has attracted much less attention, no doubt as a result of the special problems presented by the chemistry of this element.

The aim of this review is to examine in detail the known chemical compounds of radon, and to discuss possible directions of further research into the chemistry of this element.

Radon, the last (and heaviest) member of Group VIIIa (the zero group) of the Periodic Table, is unique among the inert gases in not having stable isotopes. The presence of isotopes of the element "eka-xenon" in natural radioactive series was established shortly after the discovery of radioactivity. In 1899 Marie Curie found[12] that air which has been in contact with a radium compound acquires a substantial amount of radioactivity. Rutherford and Owens[13] measured the activity of thorium salts, and noted a lack of reproducibility in the electrometer readings which Rutherford ascribed to the diffusion of a gaseous radioactive substance evolved from the thorium samples. Somewhat later, Dorn observed a similar phenomenon in a study[14] of radium-containing barium salts.

Later work showed that these gaseous radioactive substances, which had been called radium and thorium emanations (from the Latin *emanatio*, discharge), are inert gases with a high molecular weight. A third radioactive gas, evolved from actinium preparations, was discovered (independently) by Giesel[15] and Debierne[16]. Shortly after the detection of the radioactive emanations from radium and thorium their chemical nature was studied in depth[17,18], using the strongest possible oxidising or reducing conditions in order to induce compound formation.

Thus, Rutherford and Soddy[17] passed thorium emanation over platinum or palladium black, lead chromate, zinc dust, and magnesium powder (at red heat) using air, hydrogen, or carbon dioxide as the carrier gas. They failed to detect any chemical reaction. Similar results were obtained by Ramsay and Soddy[18] after lengthy exposure of a mixture of radium emanation and oxygen to an electric discharge, and also after passing radium emanation over magnesium oxide at red heat.

Table 1. Radon isotopes[19].

Isotope	Type of reaction	$T_{1/2}$	Nuclear reactions yielding the given nucleus
^{202}Rn	α	13 s	^{197}Au—^{14}N—9 *n*; Pt(^{16}O); Hg(^{12}C); ^{197}Au(^{16}O)
^{203}Rn	α	45 s	^{197}Au—^{14}N—8 *n*; Pt(^{16}O); Hg(^{12}C); Au(^{14}N)
^{203m}Rn	α	28 s	^{197}Au—^{14}N—8 *n*; Pt(^{16}O); Hg(^{12}C)
^{204}Rn	α	75 s	Hg(^{12}C); ^{197}Au(^{16}O); Pt(^{16}O); ^{197}Au—^{14}N—7 *n*
^{205}Rn	α	1.8 min	^{197}Au(^{16}O); Tl(^{12}C)
^{206}Rn	α(65%), ε(35%)	6.5 min	^{197}Au—^{14}N—5 *n*; Pb(^{12}C); Hg(^{12}C); Pt(^{16}O); Tl(^{12}C); ^{197}Au(^{16}O)
^{207}Rn	α(4%), ε(96%)	10 min	^{197}Au—^{14}N—4 *n*; Hg(^{12}C); Pt(^{16}O)
^{208}Rn	α(20%), ε(80%)	21 min	^{232}Th(*p*); ^{197}Au—^{14}N—3 *n*
^{209}Rn	α(17%), ε(83%)	30 min	^{232}Th(*p*); ^{213}Ra(2,7 min)α
^{210}Rn	α(96%), ε(4%)	2,42 h	^{232}Th(*p*)
^{211}Rn	α(26%), ε(74%)	15 h	^{232}Th(*p*)
^{212}Rn	α	25 min	^{232}Th(*p*); ^{212}Fr (19.3 min) ε
^{213}Rn	α	—	^{209}Bi(^{12}C); Pb(^{12}C)
^{215}Rn	α	10^{-6} s	^{227}U (1,3 min)α; ^{219}Ra (1 ms) α
^{216}Rn	α	$4{,}5\cdot10^{-5}$ s	^{238}U α..., ^{220}Ra (10^{-2} s)α; ^{228}U (9,1 min)α, ε
^{217}Rn	α	$5.4\cdot10^{-4}$ s	^{229}U (58 min)α; ^{221}Ra (31 s)α
^{218}Rn	α	0.035 s	^{222}Ra (38 s)α
^{219}Rn(An)	α(β⁻)	4.00 s	^{223}Ra (11,2 day)α; ^{219}At (0,9 min) β⁻; ^{227}Th (18,2 day)α...
^{220}Rn(Tn)	α	51 s	^{228}Th (1,9 year)α
^{221}Rn	α(20%), β⁻(80%)	25 min	^{232}Th(*p*)
^{222}Rn(Rn)	α	3.825 day	^{230}U (21) day)α; ^{238}U α... ^{226}Ra (1622 year)α
^{223}Rn	β⁻	43 min	^{222}Rn—*n*—γ; ^{232}Th(*p*)
^{224}Rn	β⁻	1.9 h	^{232}Th(*p*)

This degree of chemical inertness was known only in gases of the "argon family", discovered shortly before radioactivity. There were therefore strong reasons for assigning the radioactive emanations to the zero group of the Periodic Table.

The term "emanation" was used for a long time as a "combined" name for the elements of atomic number 86, though even in 1912 Ramsay had proposed the name "niton", by analogy with the names of the inert gases, in order to stress the position of element 86 in the Periodic Table. In 1923 this element was given the name "radon" in keeping with international chemical nomenclature (from its longest-lived natural isotope ^{222}Rn, $T_{\frac{1}{2}} = 3.825$ days, formed by α-disintegration of radium), and the other two natural isotopes thoron Tn and actinon An became ^{220}Rn and ^{219}Rn respectively.

The nuclear characteristics of the radon isotopes known at present are summarised in Table 1 (taken from Ref. 19).

II. PHYSICAL PROPERTIES

Under normal conditions radon is a colourless monatomic gas. The earliest measurements on radon samples prepared by gas diffusion gave seriously inconsistent values for the density and the atomic weight of this element: for example, atomic weights in the range 40–234 a.m.u. were reported. Later measurements by Debierne[21], using the diffusion method, gave an atomic weight of 220–221 a.m.u. for radon, in good agreement with the value obtained by Gray and Ramsay[22] by density measurements, using a specially designed buoyancy microbalance in which small volumes (0.1 mm^3) of radon could be weighed with an error not greater than 1%. The density of gaseous radon measured in this way was 9.727×10^{-3} g cm^{-3}, from which the atomic weight of radon was calculated as 222.4 a.m.u. Liquid radon is a colourless phosphorescent substance having a density[3,20] of 5.7 g cm^{-3}. The other physical properties of radon are listed in Table 2.

Table 2. Physical properties of radon.

Parameter	Value
Boiling point, K	208 [23]
Melting point, K	202 [24]; 160 [25]
Critical temperature, K	377.5 [24]
Critical pressure, Pa	$6.12 \cdot 10^6$ [24]
Molar heat of melting, kJ	2.717 [24]
Molar heat of evaporation, kJ	16.553* [27]; 18,338** [27] 19.228* [28]
Diameter of molecule, Å	3.64 [27]; 3,70 [29]
Viscosity at 273 K, Pa s	$2.13 \cdot 10^{-5}$ [30]
at T_{crit}, Pa s	$2.954 \cdot 10^{-5}$ [30]
Absorption cross-section for thermal neutrons (^{222}Rn), barn	0,72 [31]

*Calculated from the temperature dependence of the vapour pressure.
**Calculated by Trouton's rule.

Radon is sparingly soluble in water, its solubility being higher than that of the higher inert gases. The solubility of radon in water has been measured at low temperatures[32–35], and found to be lowered by the presence of various salts[36,37]. A study[36] of the distribution of radon between carbon tetrachloride and calcium chloride solutions of different concentration has shown that the decrease in solubility (salting-out effect) is due to the change in the activity of water in solution, which affects the hydration of the radon atoms.

Radon is appreciably more soluble in organic liquids than in water[35,37,38]. The solubility in alcohols and in fatty acids has been found[39,40] to increase with the number of the homologous group in the solvent molecule.

III. CLATHRATE COMPOUNDS OF RADON

The many unsuccessful attempts at preparing compounds of Group 0 elements led to the widespread belief (among chemists) in the absolute chemical inertness of these elements[21,41,42]. Theoretical calculations of the heats of formation of hypothetical halides and oxides of the inert gases, based on a Born cycle, confirmed that these compounds cannot be formed because all the reactions which might lead to them are strongly endothermic[43]. Only for radon fluoride was a heat of formation of ~41.8 kJ $mole^{-1}$ obtained. Thus it appeared useless, at the time, to search for compounds in which the inert gases are held by an ionic or covalent bond.

However, many compounds formed by van der Waals forces are known in chemistry. Compounds of this type involving the inert gases have been known for a long time: they include argon hydrate, discovered by Villard[44], and the hydrates of krypton[45] and xenon[46], discovered by Forcrand. All these compounds were obtained by compressing the inert gas (over water) to a pressure in excess of the dissociation pressure of the hydrate at the experimental temperature: thus, according to Forcrand, the dissociation pressure of argon hydrate at 273 K is 9.61×10^6 Pa, that of krypton hydrate is 1.42×10^6 Pa, and that of xenon hydrate is 1.13×10^6 Pa. The exact composition of these compounds was not determined at the time, but on general grounds it was assumed to be $Y_b \cdot 6H_2O$, where Y_b is an atom of the inert gas[47,48].

There can be no doubt about the existence of a similar compound of radon. However, its detection by the conventional method (change in vapour pressure) would require an impossibly large amount of radon.

Table 3. Stability of the hypothetical hexahydrates $A \cdot 6H_2O$.[42]

A	$10^{-25}\alpha$	$10^{-18}\mu$	I, kJ $mole^{-1}$	p, Pa
H_2S	37.8	0.93	100	95 980
Cl_2	46.1	0.23	127	33 730
Rn	54.2	0	103	39 990
SO_2	37.2	1.6	128	33 320

A new method of preparing and studying the molecular compounds of the inert gases, based on the phenomenon of isomorphous co-crystallisation, was proposed by Nikitin[42]. The method consists in co-precipitating the experimental substance (gas) with crystals of a known molecular compound (carrier). The method allows the formation of a molecular compound of the inert gas to be studied irrespectively of its absolute concentration. Nikitin showed that if two substances have similar van der Waals force components, and similar sizes, the molecular compounds which they form with a third substance should be similar, of comparable stability, and able to form mixed crystals. This rule can be used to define series of analogues among substances giving rise to molecular compounds.

Thus, by comparing the molecular characteristics of known hydrates with those of hydrates which had not yet been prepared (including that of radon) Nikitin concluded that the stability of radon hydrate should be of the same order as the stabilities of the hydrates of chlorine and sulphur dioxide, and significantly higher than the stability of the hydrate of hydrogen sulphide.

Indeed, in a study of the behaviour of radon during the deposition of SO_2 and H_2S hydrates Nikitin[42] demonstrated the formation of radon hydrate, co-precipitated isomorphously with the above hydrates. By using ultramicroscopic amounts of radon (~10^{-11} g) Nikitin was able to study the distribution of the element between the gas phase and the crystals of SO_2 and H_2S hydrates at a temperature (269.6 K) below the eutectic points of the SO_2–H_2O (270.5 K) and H_2S–H_2O (272.7 K) systems. The distribution coefficient of radon was found to be a constant irrespective of the direction from which equilibrium had been approached and of the relative volumes of solid and of gaseous phase. This demonstrated the isomorphous incorporation of radon into the lattice of SO_2 and H_2S hydrates as a radon hydrate of similar composition ($Rn \cdot 6H_2O$).

The relative values of the dissociation pressure of the inert gas hydrates show that the stability of these compounds increases with the atomic number of the inert gas (see Table 4): this suggests that polarisability effects are dominant in determining the stability of molecular hydrates. A method of separating the inert gases can be based on the difference between their dissociation pressures[42].

Table 4. Relative stability of the inert gas hydrates[42].

Inert gas	$10^{25}\alpha$	I, kJ mole^{-1}	$10^{8}r$, cm	$10^{-4}P_{diss}$, Pa
Rn	54.2	103	2.2	3.92
Xe	40.0	117	2.18	$1.13 \cdot 10^{2}$
Kr	24.6	134	1.98	$1.42 \cdot 10^{2}$
Ar	16.3	151	1.82	$9.66 \cdot 10^{2}$
Ne	3.9	207	1.6	—

Molecular compounds of the inert gases other than the hydrates have also been prepared by isomorphous co-crystallisation, including compounds of radon with phenol ($Y_b \cdot 3C_6H_5OH$), toluene ($Y_b \cdot 2C_6H_5CH_3$), and *para*-chlorophenol ($Y_b \cdot 3p\text{-}ClC_6H_4OH$).[42] Attempts to prepare molecular compounds of radon with aluminium halides, analogous to the hydrogen sulphide compounds $AlBr_3 \cdot H_2S$ and $AlCl_3 \cdot H_2S$, were unsuccessful[42].

According to current views on the structure of clathrate compounds[49–51] these materials should be treated as "intercalation" compounds, in which the included gas atoms or molecules are held by van der Waals forces in holes of the crystal lattice of the "host" substance.

IV. STABILITY OF RADON COMPOUNDS

The rapid development of the chemistry of the inert gases began with the discovery, in 1962, of the xenon compounds[1]. Within a relatively short time many compounds of different members of this group of elements (though mostly of xenon) had been prepared and studied in detail. Advances in radon chemistry were on a far more modest scale: only the lower fluoride of radon (RnF_2) and some of its complexes are known at present.

A comparison of the stabilities of compounds of the various inert gases suggests that the chemistry of radon should be at least as varied as the chemistry of the lighter inert gases (in particular, xenon). Thus, the heats of formation of argon, krypton, and xenon fluorides show a clear tendency for the stability of the fluoride to increase with the atomic number of the inert gas. This is ascribed to the increase in the ionisation potential from argon to krypton and xenon (see Table 5). Hence the radon fluorides should be even more stable than the corresponding xenon compounds.

Table 5. Ionisation potentials of the inert gases[62].

Element	He	Ne	Ar	Kr	Xe	Rn
$10^{-3}I$, kJ mole^{-1}	2.371	2.079	1.519	1.350	1.170	1.034

Quantum-mechanical calculations[52] of the bond ionicity and of the stability of the inert gas halides (Table 6) show an increase in the heat of formation with the atomic number of the inert gas and with the electronegativity of the ligands. The heats of formation of the radon compounds were not calculated because the ionisation potential of the element was not adequately known, but the existence of the compounds RnF_4, RnF_2, and $RnCl_2$ was thought to be possible[52].

Table 6. Bond ionicity (a), dissociation energy (E_{diss}), and heat of formation (ΔH_f°) of some inert gas halides[81,116].

Halide	a, %	E_{diss}, kJ mole^{-1}	ΔH_f^0, kJ mole^{-1}	Halide	a, %	E_{diss}, kJ mole^{-1}	ΔH_f^0, kJ mole^{-1}
XeF_4	58	208.0	−515	$KrCl_4$	37	−24.0	571
KrF_4	47	78.7	−2	XeF_2	63	101.3	−46
ArF_4	53	46.1	225	KrF_2	63	59.0	22
NeF_4	33	−452.0	2123	$XeCl_2$	54	29.7	180
$XeCl_4$	45	66.2	213				

Similar conclusions were reached[53] in a comparison of the electronegativities of the inert gas atoms and of the ligands, which led to the following stability sequences for the compounds of the group zero elements: radon fluoride > xenon fluoride > krypton fluoride; xenon fluoride > xenon oxide > xenon chloride.

Table 7. Electronegativity of the inert gases, halogens, and oxygen[8].

Element	κ	Element	κ
He	4.53	F	3.98
Ne	3.98	Cl	3.16
Ar	2.91	Br	2.96
Kr	2.58	I	2.66
Xe	2.24	O	3.44
Rn	1.98		

The electronegativities of the inert gases, halogens, and oxygen are listed in Table 7.

These qualitative estimates of the stability of the radon halides were confirmed by thermodynamic calculations of the heat of formation of the compounds. Thus, by using

Pitzer's method[54] Vasilesku[55] was able to calculate the heats of formation of the radon fluorides and chlorides, and he concluded that the chlorides as well as the fluorides of radon are thermodynamically stable. The calculation was based on the iso-electronicity principle, according to which compounds with the same number of valence electrons have similar structures and bond dissociation energies (examples of iso-electronic pairs are ZeF_2 and IF_2^-, XeF_4 and IF_4^-, XeO_3 and IO_3^-, etc.). By using this principle we can treat the halogen monofluorides as pseudo-inert gas atoms. The enthalpy of formation of the inert gas halide XY_bX (where Y_b is an inert gas atom and X is a halogen) can therefore be related to the heats of formation of the halides of other group zero elements or to the heats of formation of their iso-electronic inter-halogen compounds by the equation

$$\Delta H_{ab}=\Delta H_a+\Delta I_{ab},$$

where ΔH_{ab} is the heat of formation of Y_bX_2, ΔH_a is the heat of the reaction $Y_a + X_2 = Y_aX_2$, and ΔI_{ab} is the difference between the ionisation potentials of the central atoms in Y_bX_2 and Y_aX_2. The heats of formation of the radon halides calculated[55] by this equation are given in Table 8.

Table 8. Heat of formation of some radon halides[8].

Standard compound	$10^{-3}\Delta I_{ab}$, kJ mole^{-1}	$10^{-3}\Delta H_a$, kJ mole^{-1}	Radon compound	ΔH_f^0, kJ mole^{-1}
ClF_3	2.21	−1.06	RnF_2	−314
BrF_3	1.05	−2.03	RnF_2	−297
XeF_2	1.39	−1.54	RnF_2	−314
XeF_2	1.39	−2.17	RnF_4	−360
ICl_3	−0.29	−0.61	$RnCl_2$	−31.8

More accurate values of the heat of formation of the radon fluorides, calculated by the same method but using more reliable values of the heats of formation of the xenon fluorides and of the ionisation potential of radon, are given in Ref.11: $\Delta H_f^\circ(RnF_2)_g = -240$ kJ mole^{-1}, $\Delta H_f^\circ(RnF_4)_g = -340$ kJ mole^{-1}, and $\Delta H_f^\circ(RnF_6)_g = -412$ kJ mole^{-1}.

Radon octafluoride should be much less stable than the hexafluoride[56], because the transition from the fifth to the sixth period of elements is accompanied by a sharp fall in the stability of the higher-valency compounds, due to the "inert pair" effect. This tendency is clearly displaced by all the elements of the sixth period from thallium to polonium[57].

As regards oxygen compounds of radon, the tendency for the stability of the compound to increase with the atomic number of the inert gas suggest that oxides of six- or eight-valent radon (iso-electronic with the known astatine forms AtO_3^- and AtO_4^-) could exist[58]. The existence of radon dioxide, which should be more stable than the (unstable) xenon dioxide, is also a possibility.

Thus there are grounds for the belief that the chemistry of radon is rich and complex: however, its study so far has been complicated by many special problems.

V. SPECIAL ASPECTS OF THE STUDY OF RADON CHEMISTRY

Experimental studies of the chemistry of radon are complicated by the unfavourable nuclear characteristics of the known isotopes of this element. The longest-lived isotope (^{222}Rn) has a half-life of only 3.825 days. Working with relatively large amounts of radon (in order to make use of the standard methods of physicochemical analysis) causes difficulties, due to the high activity and to the resulting decomposition of the compounds by auto-radiolysis under the influence of the emitted α-particles. Chemical identification of the compounds in experiments with submicroscopic amounts of radon is possible only by comparing the properties and the behaviour of the radon compounds obtained with those of known compounds (of the same type) of neighbouring elements in the Periodic Table. However, we should note that the filling of the 4*f* sub-shell in elements of the sixth period could magnify the difference in properties between the compounds of elements in periods 6 and 5 (as compared with the same differences for elements of the higher periods). Thus we can expect radon to be more "metallic" than xenon[59–61], and this expectation is borne out by the ionic form of radon difluoride (in contrast to the molecular form of the corresponding fluoride of xenon)[56,60]. Quantum-mechanical calculations[60] have confirmed that an increase in the ionicity of the fluoride should occur also between radon and element 118.

These problems in the synthesis and identification of radon compounds add further complication to the study of the chemistry of radon. Adloff, in a special publication[62] on the radiochemistry of the inert gas compounds, wrote that "the chemistry of radon will never reach the same level of development as that of xenon because of the difficulties arising from the specific properties of this element".

VI. RADON COMPOUNDS

As stated above, the most useful isotope for the preparation of radon compounds and the study of their properties is the longest-lived of the isotopes (^{222}Rn). For experiments under dynamic conditions we can also use the short-lived radon isotopes ^{219}Rn and ^{220}Rn, formed by the reactions

$$^{226}Th_{1,9\ yr} \xrightarrow{\alpha} {}^{224}Ra_{3,64\ day} \xrightarrow{\alpha} {}^{220}Rn_{54,5S} \xrightarrow{\alpha} {}^{216}Po$$
$$^{227}Th_{18,17\ day} \xrightarrow{\alpha} {}^{223}Ra_{11,7\ day} \xrightarrow{\alpha} {}^{219}Rn_{3,92S} \xrightarrow{\alpha} {}^{215}Po$$

There are several methods of preparing inert gas fluorides, differing either in the choice of fluorinating agent or in the method of initiating the reaction.

Elementary fluorine, halogen fluorides, oxygen[63] or nitrogen[64] fluorides, fluorinated organic compounds[65], and some other substances have been used as fluorinating agents. The reaction can be initiated by heating the mixture, by u.v. irradiation[66,67], by an electric[68–71] or a microwave discharge[72], or by exposing the reaction mixture to γ-rays[73], to high-energy electrons[74,75], or to protons[76].

Radon fluoride can be prepared, apparently, by all these methods. It was first obtained by the most widely used of them (reaction between the inert gas and fluorine at high temperature). Heating a mixture of a small amount (1–100 μCi) of radon with fluorine at ~4×10^4 Pa pressure for 30 min at 673 K produced radon fluoride[77]. The evidence for the formation of a chemical compound was the large decrease in the volatility of radon (elemental radon sublimes easily at 195 K) produced by the admission of fluorine into the reaction vessel. The resulting fluoride had a very low volatility, and could not be sublimed in a vacuum of 10^{-4} Pa at temperatures below 500–520 K. Fluorination of a mixture of xenon and radon by a ten-fold excess of fluorine at 673 K and 3.4×10^5 Pa pressure produces di- and tetrafluorides of xenon, which readily sublime in a vacuum at 323 K, and radon fluoride which is fully retained in the reaction vessel[52]. However, when the experiment was repeated with a 100-fold excess of fluorine (573 K, 9.8×10^6 Pa) a significant amount

of radon was distilled at room temperature together with the xenon hexafluoride which was formed under these conditions[5]. The radon fluorides obtained in this work were not identified: the only comment[77] was that the product can be quantitatively reduced by hydrogen at 773 K. Micro-quantities of radon fluoride do not show any radiation-induced decomposition[77].

Chemical combination of radon by reacting with ClF_3, KrF_2, or xenon fluoride at room temperature has been reported[5], and also by reacting with oxygen monofluoride at 173 K.[78] These reactions can take place in metal, quartz, or Teflon vessels, but the reaction in a Teflon vessel yields a more volatile compound: the product of the reaction in a glass vessel is less volatile, and a still less volatile product is obtained in a metal vessel. These observations show that the surface of the reaction vessel plays an important role in the synthesis of radon fluoride.

Sufficiently large samples of radon react with liquid fluorine or solid ClF_3 (but not with chlorine) under the influence of the intrinsic α-radiation to give an involatile product. Unfortunately, a detailed description of these experiments[5] has not yet been published.

The oxidation of microgramme quantities of radon with liquid BrF_3, BrF_5, or ClF_3 also yields involatile forms of radon[61]. Between 0.12 and 0.32 Ci of radon was condensed at 73 K in a reaction vessel containing the freshly prepared fluorine halide, the mixture was thawed out, and it was allowed to warm up to room temperature over 1.5 h. Under these conditions the radon was concentrated in the lower part of the reaction vessel, and the fluorine halide which was pumped out was inactive. Dilution of an aliquot of the solution (containing 15 mCi of radon per mole of BrF_3) with fresh bromine trifluoride caused a change in specific activity strictly related to the dilution. The solutions could be centrifuged and decanted without loss of radon. The solid obtained by evaporating the solution to dryness was not identified, but the similarity between its hydrolysis and that of xenon difluoride was pointed out. It was suggested[61] that the radon is present as Rn^{2+} cations in these solutions.

The same method was used to prepare stable solutions of oxidised radon in a large number of non-aqueous solvents[79]: ClF, ClF_3, ClF_5, BrF_3, BrF_5, IF_7, an equimolar mixture of bromine and BrF_3, solutions of BrF_3 in HF and in IF_5, of BrF_5, in HF, and of K_2NiF_6 in HF. The use of arsenic, antimony, or iodine pentoxides as fluorinating agents, like the use of hydrogen fluoride, did not yield radon compounds. These observations allowed an estimate to be made[79] of the free energy of formation of radon fluoride, which must lie between the highest value of the reduction energy in the series of fluorides which oxidise radon [$E(BrF_3)$ = 167 kJ mole^{-1}] and the lowest value in the series of fluorides which fail to oxidise it [$E(AsF_5)$ = 256 kJ mole^{-1}]. When recalculated for the standard state this estimate becomes 121–214 kJ mole^{-1}.

The electro-migration of the radon compound in various solutions was studied in order to determine the charge and the chemical properties of the oxidised forms of radon[79]. The results were surprising. In pure BrF_3 solutions the radon migrates only to the cathode, but it is not discharged and it accumulates in the cathode compartment. Evidently in this solution the radon fluoride is ionised as follows[80].

$$RnF_2 \rightleftarrows RnF^+ + F^-$$
$$RnF^+ \rightleftarrows Rn^{2+} + F^- .$$

In solutions of BrF_3 in HF small quantities of radon are found in the anode compartment, and in a solution of BrF_3 in IF_5 no migration is observed. However, by saturating this solution with a strong electrolyte (KF or CsF) both cationic and anionic forms of radon are produced. This behaviour can be explained by assuming that the radon fluoride (for example, RnF_2) behaves as a Lewis base towards BrF_3 (i.e. as a donor of fluoride ions), and as a Lewis acid (i.e. as an acceptor of fluoride ions) towards compounds with a strongly developed donor function such as KF:

$$RnF_2 + BrF_3 \rightleftarrows RnF^+ + BrF_4^-$$
$$RnF_2 + KF \rightleftarrows K^+ + RnF_3^- .$$

Processes of this type are known for the fluoride of many elements in solutions of BF_3, BrF_3, BrF_5, ClF_3, etc.[81]

These workers assumed that the most likely product of the interaction between radon and fluorine or other fluorinating agents is radon difluoride, though no strict proof was given. Attempts to analyse the radon fluoride mass-spectrometrically were unsuccessful: no peaks could be recorded other than those for the full decomposition products (radon and fluorine)[79].

As stated above, one way of determining the composition of the resulting radon compounds is to compare their properties with those of the known xenon compounds. This approach has been used[82,83] to identify the chemical forms of radon produced by oxidation with strong fluorinating agents. The co-precipitation of the resulting radon fluoride with the xenon fluorides and their derivatives was studied in a special series of experiments. The macro-components were molecular crystals of the xenon fluorides themselves (XeF_2 and XeF_4), adducts of xenon difluoride and iodine pentafluoride ($XeF_2 \cdot 2IF_5$), or ionic crystals of a fluorine–xenon salt ($XeF^+Sb_2F_{11}^-$), and the solvent was iodine pentafluoride or bromine pentafluoride. The radon fluoride was prepared by treating radon with elemental fluorine and bromine pentafluoride, or with xenon di- and tetrafluoride or their solutions in iodine pentafluoride[82] or in bromine pentafluoride[83]. The co-crystallisation experiments showed that whatever the choice of fluorinating agent the radon compound obtained can be incorporated in the lattice of both molecular (XeF_2, $XeF_2 \cdot 2IF_5$)[58] and ionic compounds of bivalent xenon ($XeF^+Sb_2F_{11}^-$),[59] but not in quadrivalent xenon compounds. This suggests a similarity, both chemical and structural, between the radon compound and xenon difluoride.

Only the lower fluoride of radon is formed, apparently, because of the appearance of stable complexes of the $RnF^+MF_6^-$ type on the (fluoridised) metal surface of the reaction vessel, which prevents further fluoridation. The formation of complex fluorides is known to cause a substantial increase in the stability of inert gas fluorides. Thus, in contrast to krypton difluoride (which is unstable at room temperature), its adducts with antimony pentafluoride $KrF^+SbF_6^-$ are stable up to 353 K, and the $KrF^+Sb_2F_{11}^-$ adducts are stable up to 323 K.[84] The energy of the Kr–F bond is increased from 48 kJ mole^{-1} in KrF_2 to 135 kJ mole^{-1} in $KrF^+SbF_6^-$.[85]

Among the xenon compounds the tendency to form these adducts is more marked in the difluoride than in the tetrafluoride. The same is true, apparently, in the case of radon: furthermore, the stability of the radon double fluorides can be expected to be very much greater than that of the corresponding xenon compounds.

The radon double fluorides $RnF^+MF_6^-$ and $RnF^+M_2F_{11}^-$ can also be formed by treating radon with oxidising agents such as ClF_2SbF_6, BrF_2SbF_6, $BrF_4Sb_2F_{11}$, $IF_4(SbF_6)_3$, BrF_2BrF_6,[86] and O_2SbF_6.[87] We shall discuss these reactions and their potential practical applications in the next Section.

All attempts to prepare radon compounds other than fluorides have been unsuccessful. A study of the interaction (both thermal and photochemical) of radon with chlorine gave

inconclusive results[88]. No definite proof of compound formation was obtained in attempted reactions between radon and oxygen, ozone, or iodine monochloride[88], even when u.v. radiation and electrical or microwave discharges were used as reaction initiators[88,89]. The application of electrical or microwave discharges caused fixation of the radon on the walls of the quartz reaction vessel, possibly through the formation of very stable radonates. Thus, the radon daughter products ^{214}Bi, ^{218}Po, and ^{214}Pb are evolved when the vessel is heated to 873 K, but radon itself remains bound to the surface. However, the possibility of chemical stabilisation of the radon through the formation of oxides or silicates is not excluded[88].

VII. RADIOCHEMICAL SYNTHESIS OF RADON COMPOUNDS

In addition to the classical methods of synthesis, radiation-chemical methods and methods based on the chemical after-effects of nuclear reactions have been used in the preparation of compounds of the inert gases (β^-, β^+, and α disintegration, electron capture, isomeric transition, fission reactions, etc.). By using some of these reactions we can not only prepare known compounds but also (in some cases) predict the synthesis of new compounds.

The processes which have been most widely used in the synthesis of inert gas compounds involve the β^- disintegration of halogens incorporated in various compounds. The chemical reactions occurring during the β disintegration of atoms in molecular systems are the after-effects of nuclear, atomic, and molecular processes. The composition and charge of the nucleus (and, therefore, its nature) are altered by nucleonic processes such as the conversion of a neutron into a proton or a proton into a neutron. At the atomic level these processes can be described as

$$[^AM_z]^q \xrightarrow{\beta^-} [^AN_{z+1}]^{q+1};$$
$$[^AM_z]^q \xrightarrow{\beta^+} [^AN'_{z-1}]^{q-1},$$

where z is the charge on the nucleus, A is the mass number, M is the nucleus of the parent atom, N and N′ are nuclei of the daughter atoms, and q is the charge on the parent atom.

Table 9. Main physical characteristics* of nuclear reactions leading to the formation of radon isotopes[107].

Parent isotope	$T_{1/2}$	Type of reaction	$10^{13}E$, J	Daughter isotope	$T_{1/2}$
^{213}Ra	2.7 min	α	11.0	^{209}Rn	30 min
^{212}Fr	19.3 min	EC (56%)	—	^{212}Rn	25 min
^{219}Ra	10^{-3} s	α	12.8	^{215}Rn	10^{-6} s
^{220}Ra	10^{-2} s	α	11.9	^{216}Rn	10^{-4} s
^{221}Ra	30 s	α	10.8	^{217}Rn	10^{-3} s
^{222}Ra	38 s	α	10.4	^{218}Rn	$2\cdot10^{-3}$ s
^{223}Ra	11.2 day	α	9.2	^{219}Rn	3.92 s
^{219}At	0.9 min	β (3%)	—	^{219}Rn	3.92 s
^{224}Ra	3.64 day	α	9.1	^{220}Rn	54.5 s
^{226}Ra	1620 year	α	7.6	^{222}Rn	3.82 day

*$T_{1/2}$ is the half-life, E is the energy of the particles.

If an atom undergoing β disintegration is part of a stable molecular system, the resulting molecular system should also be stable[90] (by the iso-electronic triad rule).

Methods based on β disintegration processes have yielded a large number of inorganic (or organic) neutral (or charged) molecular forms of xenon[91–105], such as

$$*IO_3^- \xrightarrow{\beta^-} *XeO_3$$
$$*IO_4^- \xrightarrow{\beta^-} *XeO_4$$
$$*IF_5 \xrightarrow{\beta^-} *XeF_5^+$$
$$C_6H_5{}^*I \xrightarrow{\beta^-} [C_6H_5{}^*Xe]^+.$$

We should stress that organic compounds of the inert gases have not so far been prepared by classical chemical methods.

Unfortunately, in the case of radon the use of these methods is limited by the small choice of radioactive reaction chains suitable for the synthesis and identification of radon compounds. Radon isotopes are formed by the β^- disintegration of astatine, K-capture of francium isotopes, and α disintegration of radium isotopes. The main characteristics of these nuclear reactions are listed in Table 9.

We note from these results that only one case of β disintegration leading to the formation of a radon isotope is known:

$$^{219}At \xrightarrow{\beta^-} {}^{219}Rn .$$

However, the practical application of this transformation to the synthesis and study of radon compounds is complicated by the very small number of transitions leading to the formation of ^{219}At (6×10^{-5}%), the small probability of disintegration by the emission of β^- particles (3%), the very short half-lives of the parent astatine isotopes (54 s) and daughter radon isotopes (3.92 s), and our inadequate knowledge of the chemistry of astatine.

Table 10. Retention of ^{212}Rn in a chemically bound state in the disintegration of ^{212}Fr in a caesium salt[107].

Salt	Retention, %	
	in solutions	in crystals
$CsClO_4$	13±5	29±5
$CsIO_4$	11±2	25±5
$CsXeO_3F$	12±4	32±12

A more promising method of radiochemical synthesis of radon compounds is electron capture (EC) in ^{212}Fr nuclei. Following the disintegration of the nucleus by electron capture from one of the inner shells, the atoms of the daughter element acquire a large positive charge by a sequence of Auger transitions. The redistribution of this charge between the structural units of a complex molecule, and the subsequent Coulombic interaction between charges of the same sign, cause the molecule to dissociate into fragments. The neutralisation of these fragments by electrons can bring about a situation conducive to the formation of new chemical bonds. Thus, the Mössbauer effect has been used[106] to detect chemically bound forms of krypton produced by electron capture in the ^{83}Rb isotope present in isotopically enriched rubidium halides.

The possible use of electron capture processes in the synthesis of radon compounds is discussed in a study[107] of the chemical after-effects of the reaction $^{212}Fr \xrightarrow{E.C.} {}^{212}Rn$ in various caesium salts. Francium-212 ($T_{1/2}$ = 19.3 min) was obtained by irradiating a thorium target with protons of energy $E = 1.1 \times 10^{-10}$ J. The francium was removed from the target by a rapid method[108] involving co-precipitation of the francium with silicotungstic acid and separation of the francium by partition chromatography. Accumulation of

radon took place in the crystals of caesium salts containing the francium, or in solutions of these salts in 0.05 M xenon trioxide. The retention of radon in a chemically bound state is summarised in Table 10. It was suggested[107], by analogy with the xenon compounds, that the stabilisation form of the radon is the trioxide, but attempts at isolating the trioxide by coprecipitation with barium xenate or by chromatographic methods with XeO_3 as the carrier were unsuccessful.

Thus the chemical form of the trapped radon has not yet been established. However, the extent to which radon is retained in a chemically bound state strongly suggests the formation of oxygen-containing radon compounds.

The α disintegration of radium in various salts could also be a convenient radiochemical method of synthesis of radon compounds. Though α disintegration processes are far less commonly used for synthetic work than β disintegration, they have often been applied with success. For example, the formation of volatile lead compounds by the reaction $^{216}Po \xrightarrow{\alpha} {}^{212}Pb$ in the presence of gaseous hydrocarbons has been demonstrated[109]. A study of the after-effects of the α disintegration of ^{238}U in the uranylbenzoylacetonate complex has revealed a retention of $^{234}Th(UX_1)$ as high as 20–50% in acetone solution and 80–90% in the solid phase[110].

The recoil energy of the radon atoms formed by the α disintegration of radium-226 is ~1.4×10^{-14} J, and the mean free path of the radon recoil nuclei in the radium fluoride lattice is 200–300 Å.[62] Local temperature rise may favour the recombination of radon and fluorine atoms to give radon difluoride or even higher fluorides. Stabilisation of the radon formed by the α disintegration of radium in $RaCl_2$ as $RnCl_2$ cannot be excluded[62].

The first practical application of α disintegration processes to the synthesis of radon compounds was a study[111] of the stabilisation form of the radon produced by the α disintegration of ^{226}Ra in strongly oxidising solutions. The authors[111] noted differences in the amount of elemental radon extracted by hexane from a 10^{-7} M aqueous solution of $RaBr_2$ and from solutions containing HNO_3, $K_2S_2O_8$, $KMnO_4$, and other oxidising agents. A chromatographic study of the chemical state of the resulting radon indicated the formation of radon trioxide in acid media and (by analogy with the xenon compounds) $HRnO_4^-$ in alkaline solutions. However, these results were obtained only when the radon was in equilibrium with its parent ^{226}Ra: all attempts to oxidise elemental radon separated from the radium were unsuccessful[111].

On repeating these experiments it was found[112] that the whole of the "oxidised" radon can be removed from the solution by centrifuging: in other words, the decreased extractability of the radon arises not from the formation of oxygen-containing radon compounds but from the formation of ^{226}Ra colloids.

Further studies of the possible application of chemical changes accompanying the α disintegration of ^{226}Ra to the synthesis of oxygen-containing radon compounds involved the accumulation of radon in solutions of barium (radium) salts in HCl, HNO_3, HNO_3 containing XeO_3 (as a carrier for RnO_3), $HClO_4$ containing XeO_3, and also in crystals of barium (radium) perxenate[113]. However, the whole of the radon formed by α disintegration was found to be in the elemental state. The absence of oxygen-containing radon compounds was explained[113] by postulating a zero mean charge on the radon recoil nucleus.

Other types of nuclear reaction can also be used to study the possible formation of chemical compounds by radon: in particular, nuclear reactions induced by accelerated elementary particles. These methods have been used successfully in the radiochemical synthesis of compounds of the lighter inert gases. Thus, irradiation of sodium perbromate crystals with protons of energy $E = 1.6 \times 10^{-10}$ J gave high retentions of krypton in a chemically bound state, possibly through the formation of oxygen-containing compounds[114].

A very interesting study of the chemical behaviour of radon formed by irradiating uranyl sulphate crystals with high-energy protons (1.6×10^{-10} J) has been reported[107]. The retention of radon in a chemically bound state was measured by blowing off the radon after adding a reducing agent (KI solution) to the solution from which the free radon had already been removed by a stream of carrier gas[113]. The various fractions of entrained radon were collected in traps containing activated charcoal at 195 K, and the contents of all the traps were analysed in a γ spectrometer. The retention values were determined by comparing the intensities of the spectral lines given by the trap contents before and after the addition of the reducing agent (with appropriate time corrections). For the radon isotopes the retention values were less than 5%. Because of these small retentions, and of the complexity of the emission spectra, the authors[107] were unable to identify the radon compounds chemically.

VIII. POSSIBLE APPLICATIONS OF RADON COMPOUNDS

The chemistry of radon is of practical as well as theoretical interest, since it underlies the solution of one of the most fundamental problems in the protection of the environment: the purification of air from radioactive isotopes of the inert gases. The need to solve this problem has been brought into sharp focus by the growing number of nuclear power stations, and also by the serious contamination by radon of the air of uranium mines.

New developments in the chemistry of the inert gases and of inorganic fluorine-containing oxidising agents have suggested new methods of removing radioactive isotopes of the inert gases from the atmosphere. All these methods rely on chemical interaction between the inert gases and strong fluorinating oxidisers. The possibility of using these processes was first suggested[115] in 1963, and the first practical application (reported[86] in 1972) used complex salts of composition ClF_2SbF_6, BrF_2SbF_6, and $IF_4(SbF_6)_3$ as solid oxidising agents able to remove radon quantitatively from the air. In later work the choice of oxidising agents was widened very substantially. Radon can be removed from the atmosphere also by using as oxidising agents BrF_4SbF_6, O_2SbF_6, N_2FSb_6, $N_2F_3Sb_2F_{11}$,[116] $XeFSbF_6$, and some fluorine halides[117].

Among the most convenient reagents for removing radon from the atmosphere are the dioxygenyl salts (in particular, O_2SbF_6). This salt interacts with radon with evolution of oxygen according to the equation

$$Rn(g) + O_2SbF_6(s) \rightarrow RnF^+Sb_2F_{11}^-(s) + O_2(g).$$

Dioxygenyl hexafluoro-antimonate is a fairly strong oxidising agent, and it can also oxidise xenon. Using air samples artificially contaminated with ^{223}Rn and ^{133}Xe, Stein[87] showed that the radon is quantitatively adsorbed in a column (5 cm long, 6.3 mm in diameter) packed with O_2SbF_6 powder, using a gas flow rate of 45 ml min^{-1} cm^{-2}. Dilution of the dioxygenyl salt with antimony pentafluoride lowers its oxidising power below the oxidation threshold of xenon, but not of radon. It is suggested[87] that this method of chemically binding radon could find practical application for the purification of radon-contaminated air in uranium mines and for the analysis of traces of radon in the air. However, the use of this type of oxidising agent in practice is complicated by the very high reactivity of dioxygenyl salts towards common atmospheric contaminants such as water and nitrogen and carbon oxides, as well as organic compounds[118,119,120].

The interaction of radon with the salts ClF_2SbF_6 and BrF_2SbF_6 has also been studied in detail[121]. Both these oxidising agents when supported on nickel powder can effectively absorb radon from a gas stream at 213–383 K and gas flow rates up to 50 litre h^{-1}. The efficiency of radon removal is strongly dependent (as in the case of O_2SbF_6) on the presence of water vapour in the gas. Thus, the volume of air which can be freed from radon by 1 mg of oxidiser is 50–60 litre if the air is dried with P_2O_5, approximately 15 litre after drying with anhydrone, and less than 0.5 litre after drying with calcium chloride.

This very effective reaction could be used as a method of concentrating radon in the determination of ultra-micro amounts of it, and also to purify air to a residual concentration of radon isotopes not greater than 10^{-15} Ci $litre^{-1}$, i.e. well below any likely statutory threshold.

The number of radon compounds likely to find practical application is probably not limited to those listed above. Further studies of the potential uses of the compounds of the inert gases are likely to prove rewarding.

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Metal Selenocyanates

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The literature data on the complex formation reactions involving the SeCN groups in aqueous and non-aqueous solutions are surveyed. The syntheses and properties of metal selenocyanate coordination compounds are described. The bibliography includes 156 references.

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I. INTRODUCTION

Until comparatively recently, selenocyanates were virtually uninvestigated. Compounds of this class have been studied most vigorously in recent years. In view of the increased interest in complex formation reactions involving SeCN groups, we attempted to survey the available literature data on selenocyanates during the period 1970–1979. Other reviews deal with earlier studies[1-5].

II. SELENOCYANATE COMPLEXES IN SOLUTIONS

Since the SeCN groups decompose in aqueous solutions in the presence of the majority of metal ions[1], selenocyanate complexes have been studied mainly in non-aqueous media (Table 1). Naturally the nature of the solvent has a significant influence on the stability and composition of the complexes. The most stable selenocyanate complexes are formed as a rule in acetone. For example, the formation of fairly stable molybdenum complexes $MoOX_{5-n}(NCSe)_n$ and $MoO.(NCSe)_5^{2-}$ (X = Cl [17] or Br, [22] $n = 1-4$) and tungsten complexes $[WCl_{5-n}(NCSe)_n]$ ($n = 1-5$) has been demonstrated in acetone solution[23]. In other non-aqueous solvents the SeCN groups decompose fairly rapidly in the presence of molybdenum and tungsten halides.

Table 1 shows that stable complexes, among those investigated in aqueous solutions, are formed by mercury. It is therefore not surprising that mercury(II) oxide readily dissolves in solutions of potassium selenocyanate[24]. At 25 °C the heat of solution of red HgO in 1 M KNCSe solution is −103 kJ mol^{-1}.[24]

III. SELENOCYANATO-COMPOUNDS CONTAINING LIGANDS WITH ELECTRON-DONATING NITROGEN

In the presence of amines the stability of the SeCN groups increases sharply, which explains the finding that, among the selenocyanato-compounds investigated, the selenocyanato-amine compounds are the most numerous.

When pyridine was saturated with lead selenocyanate (at 80–90 °C) with subsequent cooling of the mixture, pale yellow crystals of $PbPy_2(NCSe)_2$, containing bridging SeCN groups, were precipitated[25]. The properties of the octahedral compounds $MPy_4(NCSe)_2$ (M = Mn, Co, or Ni)[26] and $MPy_2(NCSe)_2$ (M = Mn, Co, or Ni), described previously[1], were investigated[27]. The octahedral configuration of $MPy_2.(NCSe)_2$ is achieved as a result of the bridging function of the SeCN groups.

$[Co(NCSe)(NCS)Py_2]$ has been obtained by the reaction of $Co(NCS)_2$ with KNCSe in an acetone–dioxan mixture, the mixture being subsequently kept in a vacuum desiccator over calcium chloride impregnated with pyridine[28]. Treatment of $[HIr(pip)_4Cl]Cl$ (pip = piperidine) with a saturated aqueous solution of KNCSe led to the isolation of *trans*-$[HIr(pip)_4.NCSE]NCSe$.[29] The compound is diamagnetic; although the formation of the Ir–SeCN bond is characteristic of iridium, ionic NCSe groups and NCSe groups coordinated via the nitrogen atom are present in the compound.

The compound $K[CuR_2SeCN]$, where R is a pyridine-2-carboxylic acid residue, in which the copper atoms have an octahedral environment and the SeCN groups are linked to copper by weak bonds via selenium, has been synthesised[30].

Fairly numerous compounds containing 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) have been isolated in recent years, mainly from non-aqueous solutions, and investigated (Table 2).[31-46] The compound $[Fe_3(bipy)_7(NCSe)_6]$ has been obtained[47]. Its magnetic moment at 294 K is 3.24 μ_B. Its crystals have an orthorhombic lattice with the parameters $a = 21.77 \pm 0.05$ Å, $b = 25.33 \pm 0.05$ Å, $c = 13.88 \pm 0.04$ Å, and $D_m = 1.66 \pm 0.03$ g cm^{-3}; the probable space group is $Pmnb$.[47]

The complexes $Cu(bipy)(NCSe)_2$, $Cu(phen)(NCse)_2$, and $Cu(bipy)_2(NCSe)_2$ have been isolated from aqueous acetone solutions[35]. In the first two compounds the octahedral configuration of copper is achieved via bridging SeCN groups. Judging from EPR data[35], the copper in the compound $Cu(bipy)_2(NCSe)_2$ has a coordination number of 5. The complex $Mn(phen)_2(NCSe)_2$, isostructural with the corresponding thiocyanate, has also been obtained. The compound contains isoselenocyanato-groups. Its magnetic moment is 5.98 μ_B at 24 °C.[42]

The isoselenocyanato-compounds $Nb(bipy)_2(NCSe_4)$ and $Nb(DMbipy)_2(NCSe)_4$, where DMbipy = 4,4′-dimethyl-2,2′-bipyridyl, have been isolated from acetonitrile solutions, and $Ta(bipy)(NCSe)_5$ has been obtained from dichloromethane[43]. The compound $[Co(bipy)_3][Zn(NCSe)_4(bipy)]$, whose magnetic moment is 5.31 μ_B, has been obtained by the reaction of solutions containing $Co(NCSe)_2$, $Zn(NCSe)_2$, and 2,2′-bipyridyl[48]. A number of lanthanide compounds containing urotropine have been isolated from non-aqueous solutions (Table 2).

The compounds $[Ru(NH_3)_5SeCN]X_2$, where $X = ClO_4^-$, I^-, or PF_6^-, have also been described[49]. The zinc and cadmium compounds incorporating benzimidazole and its derivatives proved to be fairly stable in air[33].

Table 1. The stability constants of selenocyanate complexes in solution*.

Complex	t, °C	I	Method**	$\lg\beta_i$	References
		Solvent–H_2O			
$Hg(SeCN)_2$	25	0.3	PG	21.40	[6]
$Hg(SeCN)_3^-$	25	0.3	PG	25.60	[6]
$Hg(SeCN)Thio^+$	25	1.0	SP	27.61	[7]
$Hg(SeCN)_2(Thio)_2$	25	1.0	SP	28.51	[7]
$Hg(SeCN)_3Thio^-$	25	1.0	SP	29.15	[7]
$Cd(SeCN)^+$	25	1.0	PM	1.47	[8]
$Cd(SeCN)^+$	25	1.0	PM	1.98	[9]
$Cd(SeCN)_3^-$	25	1.0	PM	2.84	[8]
$Cd(SeCN)_4^{2-}$	25	1.0	PM	4.04	[8]
$Zn(NCSe)^+$	25	1.0	PM	0.44	[8]
$Zn(NCSe)_2$	25	1.0	PM	0.64	[8]
$Ni(NCSe)^+$	25	variable	PM	1.66	[9]
$Ni(NCSe)^+$	25	1.0	SP	0.99	[10]
$Co(NCSe)^+$	25	1.0	PM	1.49	[9]
$Tl(NCSe)_2^-$	20	1.0	PM	1.7	[11]
$Tl(NCSe)_2^-$	27	2.0	PG	0.88	[12]
$Tl(NCSe)_3^{2-}$	20	1.0	PM	1.55	[11]
$Tl(NCSe)_3^{2-}$	27	2.0	PG	1.24	[12]
$Tl(NCSe)_3^{2-}$ ***	20	2.0	PM	2.08	[11]
		Solvent–DMF			
$Zn(NCSe)^+$	20	1.0	PM	2.60	[13]
$Zn(NCSe)_2$	20	1.0	PM	4.30	[13]
$Zn(NCSe)_3^-$	20	1.0	PM	4.90	[13]
$Cd(SeCN)^+$	25	1.0	PM	2.50	[13]
$Cd(SeCN)_2$	25	1.0	PM	4.04	[13]
$Cd(SeCN)_3^-$	25	1.0	PM	5.28	[13]
$Cd(SeCN)_4^{2-}$	25	1.0	PM	6.00	[13]
$In(NCSe)^{2+}$	25	1.0	PM	7.00	[14]
$In(NCSe)_2^+$	25	1.0	PM	8.75	[14]
$In(NCSe)_3$	25	1.0	PM	10.49	[14]
$Tl(NCSe)_2^-$	20	1.7	PM	1.25	[14]
$UO_2(NCSe)^+$	room	variable	SP	2.11	[15]
$V(NCSe)^{2+}$	room	variable	SP	1.15	[16]
$MoOCl_3(NCSe)^-$	room	variable	SP	2.70	[17]
$Hf(HCSe)_6^{2-}$	room	variable	SP	7.89	[18]
$Zr(NCSe)_6^{2-}$	room	variable	SP	8.11	[18]
		Solvent–DMSO			
$In(NCSe)^{2+}$	25	1.0	PM	5.32	[14]
$In(NCSe)_2^+$	25	1.0	PM	5.87	[14]
$Bi(NCSe)^{2+}$	room	variable	SP	1.45	[19]
$Bi(NCSe)_2^+$	room	variable	SP	2.28	[19]
$Co(NCSe)^+$	room	variable	SP	1.74	[20]
$Ni(NCSe)^+$	room	variable	SP	2.41	[20]
$UO_2(NCSe)^+$	room	variable	SP	2.04	[15]
		Solvent–Acetone			
$Zn(NCSe)_4^{2-}$	room	variable	SP	11.85	[13]
$In(NCSe)_6^{3-}$	room	variable	SP	25.46	[14]
$Bi(NCSe)_6^{3-}$	room	variable	SP	14.00	[19]
$Cd(NCSe)^+$	25	1.0	PM	10.40	[13]
$Cd(NCSe)_2$	25	1.0	PM	12.28	[13]
$Cd(NCSe)_3^-$	25	1.0	PM	14.60	[13]
$Cd(NCSe)_4^{2-}$	25	1.0	PM	15.76	[13]
$In(NCSe)_6^{3-}$	25	1.0	PM	24.49	[14]
$Mn(NCSe)^+$	room	variable	SP	2.61	[21]
$Mn(NCSe)_2$	room	variable	SP	5.00	[21]
$Mn(NCSe)_3^-$	room	variable	SP	6.65	[21]
$Mn(NCSe)_4^{2-}$	room	variable	SP	7.86	[21]
$Ni(NCSe)^+$	room	variable	SP	3.84	[21]
$Ni(NCSe)_2$	room	variable	SP	7.23	[21]
$Ni(NCSe)_3^-$	room	variable	SP	10.32	[21]
$Ni(NCSe)_4^{2-}$	room	variable	SP	13.25	[21]
$Zn(NCSe)^+$	20	1.0	PM	7.30	[13]
$Zn(NCSe)_2$	20	1.0	PM	9.40	[13]
$Zn(NCSe)_3^-$	20	1.0	PM	10.78	[13]
$Zn(NCSe)_4^{2-}$	20	1.0	PM	12.25	[13]
$UO_2(NCSe)^+$	room	variable	SP	3.79	[15]
$V(NCSe)^{2+}$	room	variable	SP	2.74	[16]
$V(NCSe)_2^+$	room	variable	SP	5.92	[16]
		Solvent–CH_3CN			
$Bi(SeCN)_6^{3-}$	room	variable	SP	12.09	[19]
$Cd(NCSe)^+$	25	1.0	PM	10.41	[13]
$Cd(NCSe)_2$	25	1.0	PM	12.29	[13]
$Cd(NCSe)_3^-$	25	1.0	PM	14.62	[13]
$Cd(NCSe)_4^{2-}$	25	1.0	PM	15.78	[13]
$In(NCSe)_6^{3-}$	25	1.0	SP	24.52	[14]
$Mn(NCSe)^+$	room	variable	SP	2.62	[21]
$Mn(NCSe)_2$	room	variable	SP	5.00	[21]
$Mn(NCSe)_3^-$	room	variable	SP	6.66	[21]
$Mn(NCSe)_4^{2-}$	room	variable	SP	7.87	[21]
$Ni(NCSe)^+$	room	variable	SP	3.85	[21]
$Ni(NCSe)_2$	room	variable	PM	7.24	[21]
$Ni(NCSe)_3^-$	room	variable	PM	10.33	[21]
$Ni(NCSe)_4^{2-}$	room	variable	PM	13.27	[21]
$Zn(NCSe)^+$	20	1.0	PM	7.31	[13]
$Zn(NCSe)_2$	20	1.0	SP	9.41	[13]
$Zn(NCSe)_3^-$	20	1.0	SP	10.79	[13]
$Zn(NCSe)_4^{2-}$	20	1.0	SP	12.26	[13]
$UO_2(NCSe)^+$	room	variable	SP	3.80	[15]
$V(NCSe)^{2+}$	room	variable	SP	2.75	[16]
$V(NCSe)_2^+$	room	variable	PM	5.93	[16]

*The following abbreviations have been adopted in Table 1 and in the other tables: Thio = thiourea; DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulphoxide; I = ionic strength.

**Notation: PG = polarography; SP = spectrophotometry; PM = potentiometry.

***With addition of 50 vol % of acetone.

The interaction of alcoholic solutions of $M(NCSE)_2$ (M = Co, Ni, or Cu) with 1,1,7,7-tetraethyldiethylenetriamine [$(C_2H_5)_4$..dien] and diethylenetriamine (R) led to the solution of $[M(C_2H_5)_4dien](NCSe)_2$ (M = Co or Ni) and $[CuR_2](NCSe)_2$. In all the compounds the bond between the NCSe groups and the central atom is formed via nitrogen[45].

The kinetics of the substitution of SeCN ligands in $\{Pd..(C_2H_5)_4dien]SeCn\}^+$ by methanol and the influence of Hg^{2+} ions on the rate of the process have been investigated in methanol at 25 °C. It was established that if the SeCN group is linked to palladium via selenium, then the rate of substitution is proportional to the mercury(II) concentration; otherwise the rate is independent of [Hg(II)].[50]

The synthesis of tetragonal bipyramidal compounds $[(Cu..(Pn)_2(SeCN)]NO_3$ and $[Cu(dien)_2(SeCN)]NO_3$, where Pn = propylenediamine and dien = diethylenediamine[51], as well as $[Cu(DBen)_2(NCSE)X]$, where $X = ClO_4^-$ or NO_3^- and DBen = *N*, *N'*-dibenzylethylenediamine[52], has been described. The copper atom in $\{Cu[(C_2H_5)_4dien]NCSe\}(BPh_4)$ has a square planar environment[45].

The octahedral nickel isoselenocyanate complexes $Ni(R-NH_2)_4(NCSe)_2$ and [NiL(NCSe)]NCSe, where $R = CH_3$, $n-C_3H_7$, or $n-C_4H_9$ and L = tetraethylenepentamine, have been isolated from ethanol solutions[44]. It is of interest to note that, in the presence of piperidine, nickel(II) can form not only the octahedral compounds $[Ni(pip)_4(NCSe)_2]$ but also the pentacoordinate compound $[Ni(pip)_3(NCSe)_2]$.[26]

A series of nickel(II) and cobalt(II) compounds with *p*- and *m*-phenylenediamines (phn) have been obtained[53]. The compounds $Co(m\text{-phn})_2(NCSe)_2$, $Ni(m\text{-phn})_2(NCSe)_2$, $Ni(m\text{-phn})(NCSe)_2$, $Ni(p\text{-phn})(NCSe)_2$, and $Co(p\text{-phn})(NCSe)_2$ contain bridging SeCN groups. An octahedral structure was attributed to all the nickel(II) complexes on the basis of their effective magnetic moments[53].

The magnetic properties and EPR, infrared, and electronic spectra of the complexes $[ML_2(NCSe)_2][BPh_4]_2$, where M = Ni or Cu and L = 2,2',2''-triaminotriethylamine, have been investigated. It was established that the nickel complexes have a dimeric structure with octahedral coordination established via bridging SeCN groups, while the copper complexes have a trigonal bipyramidal structure[54].

Table 2. Fundamental vibrational frequencies of the SeCN groups (cm^{-1})*.

Compound	ν (C N	ν(CSe)	δ(SeCN)	Type of coordination of SeCN groups	Refs.
Ba(bipy)$_2$(NCSe)$_2$	2085	575	420	Ba—NCSe	[31]
Ba(phen)$_2$(NCSe)$_2$	2090	575	412	Ba—NCSe	[31]
Ba(phen)$_3$(NCSe)$_2$	2065	552	—	SeCN⁻	[31]
Ca(bipy)$_2$(NCSe)$_2$	2080,2090	588	433	Ca—NCSe	[31]
Ca(phen)$_2$(NCSe)$_2$	2075	587		Ca—NCSe	[31]
Cd(CH$_3$NH$_2$)$_2$(NCSe)$_2$	2090	580	410	Cd—NCSe	[32]
Cd(C$_2$H$_5$NH$_2$)$_2$(NCSe)$_2$	2105	585	405	Cd—NCSe	[32]
Cd(C$_3$H$_7$NH$_2$)$_2$(NCSe)$_2$	2090	577	407	Cd—NCSe	[32]
Cd(C$_4$H$_9$NH$_2$)$_2$(NCSe)$_2$	2085	—	407	Cd—NCSe	[32]
Cd(MBia)$_2$(NCSe)$_2$	2102	—	—	Cd—NCSe	[33]
Cd(MBia)$_2$(NCSe)$_2$	2112,2125	—	—	Cd—NCSe—Cd	[33]
Cd(DMBia)$_2$(NCSe)$_2$	2096, 2112,2130	—	—	Cd—NCSe—Cd	[33]
CdQ$_2$(NCSe)$_2$	2107,2120	565	407	Cd—NCSe—Cd	[34]
CdQ(NCSe)$_2$	2114,	630,	—	Cd—NCSe—Cd	[34]
CdZ$_2$(NCSe)$_2$	2125,2135	565			
	2102, 2125,2135	588	425	Cd—NCSe—Cd	[34]
Cuphen(NCSe)$_2$	2110	—	415	Cu—NCSe—Cu	[35]
Cudipy(NCSe)$_2$	2096,2117	—	432	Cu—NCSe—Cu	[35]
Cu(dipy)$_2$(NCSe)$_2$	2062,	—	443	Cu—NCSe; SeCN⁻	[35]
Cu(CH$_3$NH$_2$)$_2$(NCSe)$_2$	2073,2113	—	—	Cu—NCSe—Cu	[35]
Ga(phen)$_3$(NCSe)$_3$	2115	—	—	SeCN⁻	[36]
Ga(bipy)$_3$(NCSe)$_3$	2060	—	—	SeCN⁻	[36]
Ga(Urt)$_3$(NCSe)$_3$	2060	643	—	Ga—NCSe	[37]
Hf(bipy)$_2$(NCSe)$_4$	2082,2070	—	—	Hf—NCSe	[38]
Hf(phen)$_3$(NCSe)$_4$	2015	—	—	Hf—NCSe	[38]
In(phen)$_3$(NCSe)$_3$	2015,2060	—	—	SeCN⁻	[36]
[HIr(pip)$_4$NCSe]NCSe	2050	643,	483	Ir—NCSe, SeCN⁻	[29]
Ln(Urt)$_2$(NCSe)$_3$·nCH$_3$OH	2080,2050 2068—	641 —	—	Ln—NCSe	[39]
(Ln=Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Lu)	—2092				
Ln(bipy)$_3$(NCSe)$_3$	2035—				
(Ln=Sc, Y, La, Ce, Pr, Nd, Sm, Eu,Ga)	—2085	—	—	Ln—NCSe	[39—41]
Ln(bipy)$_2$(NCSe)$_3$·2CH$_3$OH	2033—	—	—	Ln—NCSe	[39—41]
(Ln=Sc, Y, La, Ce, Pr, Nd. Sm, Eu, Gd, Lu)	—2093				
Ln(phen)$_3$(NCSe)$_3$(Ln=Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Lu)	2040— —2060	—	—	Ln—NCSe	[39—41]
Mg(bipy)$_2$(NCSe)$_2$	2075	630	—	Mg—NCSe	[31]
Mg(phen)$_2$(NCSe)$_2$	2076	625	—	Mg—NCSe	[31]
Mn(phen)$_2$(NCSe)$_2$	2062,2065	620	433	Mn—NCSe	[42]
Nb(bipy)$_2$(NCSe)$_4$	2050,2025	698	468	Nb—NCSe	[43]
Nb(DMbipy)$_2$(NCSe)$_4$	2040, 2055,2085	695	450	Nb—NCSe	[43]
Ni(C$_4$H$_9$NH$_2$)$_4$(NCSe)$_2$	2085,2110	>580	425	Ni—NCSe	[44]
[Ni{(C$_2$H$_5$)$_4$dien}NCSe]Ph$_4$B	2094	—	420	Ni—NCSe	[45]
Ni(CH$_3$NH$_2$)$_4$(NCSe)$_2$	2100	>580	423	Ni—NCSe	[44]
Ni(C$_3$H$_7$NH$_2$)$_4$(NCSe)$_2$	2095	>580	426	Ni—NCSe	[44]
Sr(bipy)$_2$(NCSe)$_2$	2075,2125	568, 580	—	Sr—NCSe	[31]
Sr(phen)$_3$(NCSe)$_2$	2060	552	—	SeCN⁻	[31]
Ta(bipy)(NCSe)$_5$	1930	697	465	Ta—NCSe	[43]
UO$_2$(bipy)$_2$(NCSe)$_2$	2048	—	—	U—NCSe, SeCN⁻	[46]
UO$_2$(phen)$_2$(NCSe)$_2$	2051	—	—	U—NCSe, SeCN⁻	[46]
ZnQ$_2$(NCSe)$_2$	2095	680	—	Zn—NCSe	[34]
ZnZ$_2$(NCSe)$_2$	2095,2108	675	—	Zn—NCSe	[34]
Zr(bipy)$_2$(NCSe)$_4$	2010	—	—	Zr—NCSe	[38]
Zr(phen)$_3$(NCSe)$_4$	2060,2090	—	—	Zr—NCSe, SeCN⁻	[38]

* The following abbreviations have been adopted in Table 2: Q = benzoxazole; Z = 2-methylbenzoxazole; Bia = benzimidazole; MBiA = methylbenzimidazole; DMBia = dimethylbenzimidazole; Urt = urotropine; dien = diethylenediamine; Dmbipy = 4,4'-dimethyl-2,2'-bipyridyl.

Copper(II) selenocyanate complexes with diguanide (L) derivatives having the composition $[CuL_2](NCSe)_2$, in which the NCSe groups are ionic judging from infrared absorption spectra, have been studied; on the other hand, the Cu–SeCN bond is present in the compound $CuL(SeCN)_2$.[55]

The compounds $Cu(Ben)_2(SeCN)(NO_3)$ and $Ni(Ben)_2.(SeCN)(NO_3)$ have been isolated after the interaction of nickel and copper nitrates with benzylethylenediamine (Ben) in ethanol and subsequent treatment of the product with potassium selenocyanate, while the interaction with *N,N'*-dibenzylethylenediamine (DBen) led to $Ni(DBen)_2(NCSe)_2$ and $Co(DBen)_2(NCSe)_2$. It was shown that the last two complexes are octahedral, while $Cu(Ben)_2(SeCN)(NO_3)$ and $Ni(Ben)_2(SeCN)(NO_3)$ are tetrahedral[56]. Bridging SeCN groups have been detected in the compound $Cu(Ben)_2(SeCN).(NO_3)$, while the remaining complexes contain isoselenocyanato-groups[56].

The nickel and cobalt complexes of certain diamines can also be classified as isoselenocyanates: $ML_2(NCSe)_2$, where $L = NH_2NH_2$, o-$(NH)_2C_6H_4$, or ethylenediamine (En).[57] The interaction of hot solutions of $M(ClO_4)_2.6H_2O$ (M = Mn, Fe, Co, Ni, or Cu) in ethanol with LiNCSe in the presence of 2,3,5,6-tetrakis (6-methyl-2-pyridyl)pyrazine (L) led to the formation of the isoselenocyanato-compounds $ML(NCSe)_2$.[58] A series of complexes with dihydrazinophthalazine (Dhph) have been isolated from aqueous solutions: $[Cu_2(Dhph)(SeCN)_2].4H_2O$, $[M(Dhph)(SeCN)_2].2H_2O$ (M = Zn, Co, or Ni), and $[M(Dhph)(SeCN)_2]$ (M = Cd or Mn).[59] The copper complex is diamagnetic and its organic ligand has a bridging function and is bidentate, i.e. the coordination number of copper is 4. In the remaining compounds dihydrazinophthalazine is tetradentate and the coordination of the metal is 6.[59]

The compound [CoL(NCSe)]NCSe, where L is the corresponding Schiff base, has been obtained by the reaction of cobalt(II) acetate with pyridine-2-carboxaldehyde and bis-(3,3'-aminopropyl)amine in the presence of triethyl orthoformate in an atmosphere of nitrogen with subsequent addition of KNCSe.[60] A series of cobalt compounds $Co(NCSe)_2.nA$, where A = diaminobiphenyl and its derivatives, have been described. They are all high-spin compounds in which the cobalt atom has a hexacoordinate environment[61]. Isoselenocyanato-groups are present in the compounds $NiL_2.(NCSe)_2$, where L = 3,3'-bis(aminopropyl) ether, while the nickel ion has a pseudo-octahedral environment[62].

Manganese(II), cobalt(II), zinc, and cadmium compounds containing *N,N*-diethylnicotinamide (DENA) have been isolated from acetone solution: $[Ni(DENA)_2(NCSE)_2].2H_2O$,[63] $[Cd(DENA)_2(NCSe)_2$,[64] $[Zn(DENA)_2(NCSe)_2(H_2O)_2]$,[65] $Mn(DENA)_2(NCSE)_2$, $[Co(DENA)_2(NCSe)_2(H_2O)_2]$, and $[Co(DENA)_4(NCSe)_2]$.[66] The state of bivalent manganese, cobalt, nickel, zinc, and copper complexes with *N,N'* diethylnicotinamide, nicotinamide, acetamide, and propionamide in aqueous solutions and in solutions in organic solvents has been studied[67]. The cadmium complex of nicotinamide $Cd(NA)(NCSe)_2$ has also been obtained. The coordination of nicotinamide in this compound is via the nitrogen heteroatom, while the NCSe groups are also coordinated via nitrogen[68].

A series of analogues of vitamin B_{12} of the type $Co(NCSe).(OH)_2R$, where R = purine or pyrimidine derivative, have been described[69].

Manganese selenocyanate complexes with *o,o'*-, *m,m'*-, and *p,p'*-diaminobiphenyls (Q) and with *p,p'*-diaminodiphenylmethane (L) have been synthesised by adding concentrated solutions of Q or L to an alcoholic solution of $Mn(NCSe)_2$; $Mn(o,o'\text{-}Q)_2(NCSe)_2$, $Mn(m,m'\text{-}Q)_2(NCSe)_2$, $Mn(p,p'\text{-}Q)_3(NCSe)_2$, and $Mn(p,p'\text{-}L)_3(NCSe)_2$.[70] Infrared

absorption spectra and magnetic properties led to the conclusion that the manganese atom in the complexes has coordination number 6.[70]

The complexes $MnL_4.(NCSe)_2$ have been synthesised by refluxing an ethanol solution of $Mn(NCSe)_2$ with pyridine, β- and γ-picolines, 3,5-lutidine, 4-ethylpyridine, and isoquinoline. The compounds contain isoselenocyanato-groups and the manganese atom has an octahedral environment[71].

The complexes $M(BH)_2(NCSe)_2$ have been synthesised by the reaction of manganese, cobalt, nickel, and zince selenocyanates with benzoylhydrazine (BH) in ethanol or acetone. It was established that the nickel and cobalt complexes are isostructural[72]. The compounds $CdL_2(NCSe)_2$, where L = benzoxazole and its derivatives, have been isolated from non-aqueous media[34]. The compounds $Zn(Ampy)_2(NCX)_2$ (X = O or Se and Ampy = 2-aminopyridine) have been shown to be isostructural. In these compounds zinc has a tetrahedral environment and some of the aminopyridine molecules are coordinated to zinc via the nitrogen of the amino-group, while others are coordinated via the nitrogen of the heterocycle. The NCSe groups are monodentate and are linked to zinc via nitrogen[73].

New cobalt(III) chelates of the type $[CoLA_2]SeCN$, incorporating ethylenediaminobisacetylacetone (L), ethyl- or n-propyl-amine (A), and SeCN groups, have been synthesised[91].

Copper(II) compounds containing ethylenediamine (En) have been isolated from aqueous ethanol solutions: $CuEn_2.(SeCN)X$, where $X = Cl^-$, Br^-, SCN^-, or NO_3^-. The coordination polyhedron of the central atom consists of a distorted pseudosquare pyramid or a square bipyramid[75]. The interaction of $Cu(CH_3COO)_2$ with L and KNCSe, where L = β-(2-pyridyl)ethylamine or 2-pyridylmethylamine, in absolute methanol in an atmosphere of nitrogen led to the formation of the compound $CuL(NCSe)_2$, where L behaves as a tridentate ligand[76].

The interaction of $CuLCl_2$, where L = 1,4-diphenyl-2-thioammeline, with KNCSe in dry *N,N*-dimethylformamide yielded the compound $CuL(SeCN)_2$, in which the SeCN groups are coordinated via the selenium atom, while the organic ligand is coordinated via the nitrogen and sulphur atoms[77]. Tetrahedral isoselenocyanate complexes with benzimidazole (Bia) and its derivatives have been obtained from ethanol solutions: $Co(MBia)_2(NCSe)_2$, $Co(DMBia)(NCSe)_2$, and $Co(Bia)(NCSe)_2$; here the organic ligand is bound to the metal via the nitrogen atom in the 3-position in the imidazole ring[78].

Much attention has been devoted recently to the study of the cobalt(III) complexes of *trans*-dioximes having the general composition $[Co(HD)_2L(SeCN)].nH_2O$, where HD is a dimethylglyoxime residue and L = 3-cyanopyridine[79], 4-cyanopyridine, pyridine, 4-aminopyridine[80], 2-aminopyridine[81], PPh_3, $PPh_2(n\text{-}Bu)$, PPh_2Me, P(n-Bu), $P(OPh)_3$, $P(O\text{-}n\text{-}Bu)_3$, $P(OMe)_3$, $P(O\text{-}iso\text{-}Pr)_3$, 4-acetylpyridine[82], piperidine, 3-chloropyridine, NH_3, or $PrNH_2$.[83] In all these compounds the bond between the SeCN groups and the central atom is formed via selenium. They have been shown to exhibit an antibacterial activity and the spectrum of the antimicrobial activity of dioxime complexes of this type (in which L are various sulphanilamides[84,85] and sulphanilylpyridines[86-88]) has been expanded relative to the initial complexes and sulphanilylpyridines.

The complexes *trans*-$[Co(HDph)_2LNCSe].H_2O$, where HD is diphenylglyoxime, and L = *p*-aminobenzenesulphonylguanidine[89], 2-(*p*-aminobenzenesulphonyl)pyridine[88], or 4-sulphanilylpyridine[86], have been obtained. The thermal stability of the complexes with the last ligand depends on the nature of the acido-ligand X (Cl, Br, I, NCO, NCS, or NCSe), reaching a maximum in the selenocyanate complex[86].

Dinuclear complexes of the type *trans*-$[ACo(HD)_2\text{–}SeCN\text{–}Co(HD)_2SeCN]$, where HD is a dimethylglyoxyme residue and A = PPh_3, $PPh_2(n\text{-}Bu)$, $P(OPh)_3$, or $P(OCH_3)_3$, are formed in solvents with a low dielectric constant, for example in dichloromethane; in these complexes the terminal SeCN groups are coordinated to cobalt via the selenium atom regardless of the nature of A.[82] The bridged complexes $\{RCo(HL)_2\}\text{–}NCSe\text{–}\{Co(HL)_2Q\}$, where R = CH_3 or CF_3 and Q = piperidine, have been isolated from chloroform[83].

The compounds $[Co(HL)_2(NO_2)(NCSe)]$, where HL is a methylisopropylglyoxime residue[90] and the new cobalt(III) chelates $[CoZQ_2]SeCN$ (H_2Z is a tetradentate ligand consisting of the Schiff base obtained from acetylacetone and ethylenediamine, namely ethylenedi-iminobisacetylacetone, and Q are amines ($C_2H_5NH_2$, $n\text{-}C_3H_7NH_2$, or $CH_2=CH\text{–}CHNH_2$),[91] have also been obtained. The complex acid $H[Co(DH)_2.(NCSe)_2].H_2O$, which is sparingly soluble in water and is resistant to the action of inorganic acids, as well as a whole series of its salts (DH = cyclohexane-1,2-dione dioxime residue)[92] and $H[Co(HL)_2(NCSe)_2]$, where HL = diaminoglyoxime residue[93], have been isolated.

IV. HETEROLIGAND COMPOUNDS INCORPORATING LIGANDS WITH ELECTRON-DONATING OXYGEN

The majority of the compounds considered here are presented in Table 3. In all the compounds with dimethyl sulphoxide (DMSO) the latter is bound to the central atom via oxygen. On the other hand, the mode of coordination of the SeCN groups depends both on the nature of the central atom and on the composition of the complex (Table 3). In the isostructural complexes $M(DMSO)_4(NCSe)_2$ (M = Fe, Co, Mn, or Ni) the central atom has the octahedral configuration Mo_4N_2, probably with the *trans*-location of the isoselenocyanato-groups[96]. In the compound $Cd(DMSO)_2(NCSe)_2$ the cadmium atoms are linked together to infinite chains via bridging SeCN groups. The DMSO molecules complete the polyhedron to form an octahedron. The interatomic distances are Cd–Se = 2.773 Å, Cd–N = 2.26 Å, and Cd–O = 2.30 Å; the SeCN and CdNC angles are 171.5° and 172.6° respectively[100]. The compound $Pb(DMSO)_2(NCSe)_2$ apparently has an analogous structure[25]. The bonds between the SeCN groups and the central atom in the compounds $M(MFA)_4(NCSe)_2$ and $M(DMA)_4(NCSe)_2$ (M = Mn, Co, Ni, or Zn, MFA = *N*-methylformamide, and DMA = *N,N*-dimethylacetamide) are formed via nitrogen, while the organic ligand is linked via oxygen[73,101,102].

Structural study of $Ni(DMA)_4(NCSe)_2$ crystals showed that they are monoclinic and have the lattice parameters $a = 7.67$ Å, $b = 10.40$ Å, $c = 9.74$ Å, and $\gamma = 114°$. The crystals of this compound are isostructural with those of *trans*-$Ni(DMA)_4(NCSe)_2$, in which the SeCN groups are linked to nickel via nitrogen and DMA molecules are linked via oxygen[74].

The compound $Cd(DMF)_2(NCSe)_2$ has been isolated from alcoholic solutions containing $Cd(SeCN)_2$ and *N,N*-dimethylformamide (DMF). It contains bridging SeCN groups, while the bond between DMF and cadmium is formed via oxygen[103], as in the other compounds presented in Table 3. Many selenocyanato-compounds containing antipyrine (A) and diantipyrylmethane (D) are known (Table 3). In all these compounds the organic ligand is linked to the central atom via oxygen, occupying one (antipyrine) or two (diantipyrylmethane) coordination sites. Gallium and indium selenocyanate complexes containing alkyl- or aryl-phosphine oxides have also been studied[37]. Table 3 shows that in all cases

an M–NCSe bond is formed and the central atom acquires an octahedral configuration.

The extraction of uranyl selenocyanates with chloroform solutions of certain oxygen-containing organic reagents has been studied[104]. The composition of the extracted compounds has been established by the equilibrium shift method: $UO_2L_3(NCSe)_2$ (L = antipyrine, triphenylphosphine oxide, or hexamethylphosphoramide) and $UO_2L_2(NCSe)_2$ (L = diantipyrylmethane and phenyldiantipyrylmethane)[104].

Table 3. Fundamental vibrational frequencies of the SeCN groups (cm^{-1})*.

Compound	ν (CN)	ν (CSe)	δ (SeCN)	Type of coordination of SeCN groups	Refs.
$Bi(DMSO)_6(SeCN)_3$	2050, 2110	553	—	Bi—SeCN	[94]
$Bi(DMF)_3(SeCN)_3 \cdot 2DMFA$	2110, 2123	545	—	Bi—SeCN	[94]
$Bi(HMP)_3(NCSe)_3$	2100	640	—	Bi—NCSe	[95]
$Cd(DMSO)_{1/2}(SeCN)_2$	2115, 2131	580	—	Cd—SeCN	[96]
$Cd(HMP)_2(NCSe)_2$	2195, 2080	575	—	Cd—NCSe, Cd—SeCN—Cd	[97]
$Co(DMSO)_4(NCSe)_2$	2095	610	—	Co—NCSe	[96]
$Co(HMP)_2(NCSe)_2$	2082	650	425	Co—NCSe	[97]
$Cr(HMP)_3(NCSe)_3$	2080, 2095, 2110	620	405, 442	Cr—NCSe	[95]
$Fe(DMSO)_4(NCSe)_2$	2081, 2030	610	—	Fe—NCSe	[96]
$GaA_3(NCSe)_3$	2070	625	—	Ga—NCSe	[36]
$GaD(NCSe)_3$	2062, 2082, 2100	620	—	Ga—NCSe	[36]
$Ga\{OP(C_3H_7)_3\}_3(NCSe)_3$	2070, 2170	650 617	432	Ga—NCSe	[37]
$Ga\{OPPh_3\}_3(NCSe)_3$	2070, 2055	618	—	Ga—NCSe	[37]
$In(DMF)_3(NCSe)_3$	2070	618	—	In—NCSe	[36]
$In(DMSO)_3(NCSe)_3$	2065, 2080	615	—	In—NCSe	[36]
$In(HMP)_3(NCSe)_3$	2075, 2095	650	432	In—NCSe	[95]
$La(HMP)_3(NCSe)_3$	2070	605	426	La—NCSe	[95]
$LnD_2(NCSe)_3$ (Ln=Ce, La, Lu, Nd)	2050—2060	—	—	Ln—NCSe	[39]
$LnD_3(NCSe)_3$ (Ln=Ce, Pr, Eu, La, Lu, Gd, Nd, Sm)	2060—2080	—	—	Ln—NCSe	[39]
$LnD_4(NCSe)_3$ (Ln=La, Ce, Pr, Nd, Lu)	2060—2065	—	—	$SeCN^-$	[39]
$Ln(HMP)_5(NCSe)_3$(Ln=Ce, Pr, Nd)	2070—2080	605—610	~430	Ln—NCSe	[98]
$Ln(HMP)_4(NCSe)_3$(Ln=La, Sm—Lu)	2050—2090	~615	~440	Ln—NCSe	[93, 95]
$Mn(DMSO)_4(NCSe)_2$	2075	610	—	Mn—NCSe	[96]
$Mn(HMP)_2(NCSe)_2$	2065	645, 655	426, 420	Mn—NCSe	[97]
$Ni(DMSO)_4(NCSe)_2$	2098	618	—	Ni—NCSe	[96]
$Ni(HMP)_2(NCSe)_2$	2138, 2110	620	—	Ni—NCSe—Ni; Ni—NCSe	[94]
$Pb(DMSO)_2(NCSe)_2$	2096, 2141	543	403	Pb—NCSe—Pb	[25]
$Sc(HMP)_3(NCSe)_3$	2060, 2085	650	440	Sc—NCSe	[95]
$ScD_3(NCSe)_3$	2060	—	—	Sc—NCSe	[39]
$ScD_4(NCSe)_3$	2052, 2062	—	—	$SeCN^-$	[39]
$UO_2(DMSO)_3(NCSe)_2$	2046, 2069	630	—	U—NCSe	[46]
$UO_2(Diox)_3(NCSe)_2$	2050	635	—	U—NCSe	[15]
$UO_2D_2(NCSe)_2$	2060, 2070	—	—	U—NCSe	[46]
$UO_2A_3(NCSe)_2$	2055	592	—	U—NCSe	[46]
$VO(HMP)_3(NCSe)_2$	2100, 2110	—	—	V—NCSe	[99]
$YD_2(NCSe)_3$	2065	—	—	Y—NCSe	[39]
$YD_3(NCSe)_3$	2070, 2085	—	—	Y—NCSe	[39]
$YD_4(NCSe)_3$	2065	—	—	$SeCN^-$	[39]
$Y(HMP)_3(NCSe)_3$	2050, 2060, 2070	635	436	Y—NCSe	[95]
$Zn(HMP)_2(NCSe)_2$	2090	650	425	Zn—NCSe	[97]

* The following abbreviations have been adopted in Table 3: A = antipyrine; D = diantipyrylmethane; HMP = hexamethylphosphoramide; Diox = 1,4-dioxan.

Selenocyanato-compounds containing hexamethylphosphoramide (HMP) are formed readily when acetone or alcoholic solutions of the corresponding metal selenocyanates are treated with HMP [95–99] (Table 3). In all the compounds HMP is linked to the central atom via oxygen. Compounds having the composition $M(HMP)_2(NCSe)_2$ (M = Mn, Co or Zn) are isostructural. The study of the magnetic properties and the electronic absorption spectra indicated an octahedral structure of the cobalt compound. However, the nickel compound is not isostructural with the analogous cobalt, zinc, and manganese compounds. On the other hand, the magnetic moment, which amounts to 3.6 μ_B, rules out a planar structure of $Ni(HMP)_2(NCSe)_2$. Nickel in the above compound probably has a coordination number of 5 owing to the bridging SeCN groups. In air the compound readily combines with water and is converted into the dihydrate. Judging from the electronic absorption spectra and the magnetic moment (3.02 μ_B), the nickel in the compound is octahedral and the SeCN groups are *N*-linked to nickel[97]. Bridging isoselenocyanato-groups are present in $Cd(HMP)(NCSe)_2$ and the cadmium atom has a tetrahedral environment[97].

All the compounds $M(HMP)_3(NCSe)_3$ in Table 3 contain isoselenocyanato-groups. This is somewhat unexpected for bismuth, because the formation of Bi–SeCN bonds is more characteristic of this element[95,99]. Evidently the "inversion" of the bond linking the SeCN groups in this instance is due to the steric hindrance caused by hexamethylphosphoramide.

Blue crystals of $VO(HMP)_3(NCSe)_2$ have been obtained by adding an excess of KNCSe and HMP to an acetone solution of $VOCl_2$. The compound is isostructural with the analogous thiocyanate. The values of ν(VO) for the thiocyanato- and selenocyanato-compounds are the same (965 cm^{-1}), which may be regarded as proof of the *trans*-position of the HMP molecules relative to vanadyl oxygen and not of XCN groups[99]

Lanthanide selenocyanate complexes with nonamethylimidophosphoramide (NIPA) have been isolated from acetone: $Ln(NIPA)_3(NCSE)_3$ (Ln = Pr, Nd, or Sm) and $Ln_2(NIPA)_5 \cdot (NCSe)_3$ (Ln = Gd, Tb, Er, Tm, or Lu), which are isostructural with the analogous thiocyanates. As for thiocyanates, the coordination number in the selenocyanates decreases from nine (Pr, Nd, and Sm) to eight (Gd–Lu).[105]

V. COORDINATION SELENOCYANATO-COMPOUNDS OF THE ACIDO-TYPE

Coordination compounds of the acido-type containing only SeCN groups in the anion can be obtained (with the exception of the mercury compounds) solely from non-aqueous solutions. Table 4 shows that in all the compounds considered the mode of coordination of the SeCN groups most characteristic of the complex-forming metal is retained[1,109]. It is of interest that the octahedral environment of the central atom in the compounds $(UrtH)_2[M(NCSe)_4]$ (M = Co or Ni and Urt = urotropine) is achieved not only via the SeCN groups but also with the aid of the cation[106].

The compounds $[(CH_3)_4N]_4[Fe(NCSe)_6]$, $[(C_2H_5)_4N]_3 \cdot [Fe(NCSe)_5(H_2O)]$, $[C_4H_9)_4N]_2[Fe(NCSe)_4]$, and $[(C_4H_9)_4N]_3 \cdot [Fe(NCSe)_6]$, which are high-spin complexes and contain isoselenocyanato-groups, have been obtained by the method already described[110], isolated, and investigated[111]. A similar type of coordination has also been observed in the octahedral compounds $R_4[Co(NCSe)_6]$, $R_3[Fe(NCSe)_5(H_2O)]$, $R_3[V(NCSe)_6]$, $R_3[Mo(NCSe)_6]$, and $R_3[MoO(NCSe)_5]$, where $R = (C_2H_5)_4N^+$,[112] and also in $R'_3[Cr(NCSe)_6]$, where $R' = K^+$ or $(C_4H_9)_4N^+$.[113]

When $[(C_4H_9)_4N]_2Re_2Cl_8$ was allowed to react with KNCSe in ethanol or acetonitrile, it was possible to isolate the rhenium compound $[(C_4H_9)_4N]_2[Re_2(NCSe)_8]$. Judging from the wavenumber ν(CN) = 2050 cm^{-1}, the SeCN groups are linked to the rhenium atom via nitrogen[114]. In the presence of $SeCN^-$ ions, rhenium pentachloride forms polymeric complexes in acetone via bridging SeCN groups[115].

The compounds of Group V elements $K[M(NCSe)_6]$ (where M = Nb or Ta), $K_2[Nb(NCSe)_6]$, and $[Ph_4As][Ta(NCSe)_6]$ have been obtained from acetonitrile solutions[116]. It also proved possible to isolate from acetonitrile the compounds $K_2[Zr.(NCSe)_6]$, $K_2[Hf(NCSe)_6]$,[117] $[(C_2H_5)_4N]_4[Pa(NCSe)_8]$, and $[(C_2H_5)_4N]_4[U(NCSe)_8]$.[118] X-Ray diffraction study showed that the last two compounds are isostructural and belong to the tetragonal system (the lattice parameters are $a = 11.82$ Å and $c = 23.49$ Å for the first compound and $a = 11.80$ Å and $c = 23.36$ Å for the second)[118].

Table 4. Fundamental vibrational frequencies of the SeCN groups in selenocyanates of the acido-type (cm^{-1})*.

Compound	ν (CN)	ν (CSe)	δ (SeCN)	Type of coordination of SeCN groups	Refs.
$(UrtH)_2Co(NCSe)_4$	2083, 2095	—	—	Co—NCSe	[106]
$[(C_4H_9)_4N]_3[Ga(NCSe)_6]$	2075	615, 635	—	Ga—NCSe	[36]
$[Ph_4As]_3[Ga(NCSe)_6]$	2060	612	—	Ga—NCSe	[37]
$Ba[Ga(NCSe)_4]\cdot 6THF$	2075	612	440	Ga—NCSe	[37]
$[(C_4H_9)_4N]_3[Zn(NCSe)_6]$					
Ln : Dy	2047	644	434	Dy—NCSe	[107]
Er	2050	646	435	Er—NCSe	[107]
Nd	2058	615	428	Nd—NCSe	[107]
Pr	2058	613	425	Pr—NCSe	[107]
Ho	2048	642	433	Ho—NCSe	[107]
$[(C_2H_5)_4N]_2[MoO(NCSe)_5]$	2060	650	470	Mo—NCSe	[17]
$K_2Nb(NCSe)_6$	1985, 2070	710, 740	490, 459	Nb—NCSe	[92]
$KNb(NCSe)_6$	1918, 1961	740, 972	449, 459	Nb—NCSe	[92]
$(UrtH)_2Ni(NCSe)_4$	2098, 2105	606	438, 426, 431	Ni—NCSe	[106]
$KTa(NCSe)_6$	1925, 1972 2001, 2075	763, 779	449, 455	Ta—NCSe	[92]
$Li_3[Bi(SeCN)_6]\cdot 3Act$	2110	545	405	Bi—SeCN	[108]
$[Ph_4As][Ta(NCSe)_6]$	1925, 1981, 2035	749	468	Ta—NCSe	[92]
$Na_3[Bi(SeCN)_6]$	2073, 2085, 2110	535, 548	405	Bi—SeCN	[108]
$Ca_3[Bi(SeCN)_6]_2\cdot 10Diox$	2112	—	400	Bi—SeCN	[108]
$Sr_3[Bi(SeCN)_6]_2\cdot 2Diox$	2100	532	400	Bi—SeCN	[108]
$Mn_3[Bi(SeCN)_6]_2\cdot 10Diox$	2120	530	400	Bi—SeCN	[108]
$KBa[Bi(SeCN)_6]\cdot 2Act$	2093	545, 557	500	Bi—SeCN	[108]
$Li_2Bi(SeCN)_5\cdot 3Diox$	2085, 2130	545, 573	403, 455	Bi—SeCN—Bi	[108]
$Mg_3[Bi(SeCN)_6]_2\cdot 9Diox$	2131	—	406	Bi—SeCN—Bi	[108]
$Pb[Hg(SeCN)_3]_2$	2124, 2140, 2158	535, 545	405	Hg—SeCN—Hg	[93]
$KCd(SeCN)_3$	2096, 2113, 2122, 2132	540, 547	405, 420	Cd—SeCN—Cd	[93]
$KHg(SeCN)_3$	2122, 2142	535, 543	—	Hg—SeCN—Hg	[93]
$KPb(SeCN)_3$	2080, 2118, 2140	532, 579	420	Pb—SeCN—Pb	[25]
$[(C_4H_9)_4N]_3[UO_2(NCSe)_5]$	2050, 2070	610	—	U—NCSe	[15]
$[(C_2H_5)_4N]_3[UO_2(NCSe)_5]$	2040, 2060	625	—	U—NCSe	[15]

* The following abbreviations have been adopted in Table 4: Urt = urotropine; Diox = 1,4-dioxan; Act = acetone.

The uranyl selenocyanates $[(C_4H_9)_4N]_3[UO_2(NCSe)_5]$ and $[(C_2H_5)_4N]_3[UO_2(NCSe)_5]$ were isolated from methanol[15]. All the compounds mentioned above contain isoselenocyanato-groups. The formation of the Bi–SeCN bond is more characteristic of bismuth selenocyanates; bridging selenocyanato-groups are present in the mercury, lead, and cadmium compounds (Table 4).

Among heteroligand complexes of the acido-type, the mercury and cadmium compounds have been studied most thoroughly (Table 5). The compounds $K_2[Cd(SeCN_2)SCN)_2]$, $K_4[Cd(SeCN)_4(SCN)_2].0.5$ Act, $K_2[Cd(SeCN)_2(Hal)_2]$ (where Hal = Cl or Br), $K_4[Cd(SeCN)_4I_2].0.5$ Act, and $K_2[Cd(SeCN)_3I].$ Act were synthesised by crystallisation from acetone solutions containing CdX_2 ($X = SCN^-$, Cl^-, Br^-, or I^-) and KNCSe in proportions of 1 : 2 or 1 : 4 [120,124] [Act = acetone (Ed. of Translation)]. It follows from infrared spectroscopic data that $K_2[Cd(SeCN)_2(SCN)_2]$ contains both terminal Cd–SeCN bonds and bridging Cd–SeCN–Cd linkages[120]. Bridging SeCN groups are also present in $K_2[Cd(SeCN)_2(Hal)_2]$, while in the compound $K_4[Cd(SeCN)_4I_2]$ the SeCN groups are linked to the central atom via selenium[120,124]. Cadmium compounds incorporating together with SeCN groups the non-linear $N(CN)_2$ and $C(CN)_3$ groups have also been obtained (Table 5). All these compounds except $K_2\{Cd[C(CN)_3]_2.(NCSe)_2\}$ contain isoselenocyanato-groups. The last compound contains bridging SeCN groups.

The mercury compounds $K_2[Hg(SeCN)_2A_2]$, where $A = Br^-$, I^-, or SCN^-, have been isolated from acetone[124]. SeCN groups linked to mercury via selenium are present in these complexes and also in $Ba[Hg(SeCN)_2(SCN)_2].2Act$, but the presence of SeCN bridges may be suggested in $K_2[Hg(SeCN)_2.Br_2]$, in view of the band at 2138 cm^{-1}.[122] Bridging SeCN groups are also present in the compound $Ba[Hg(SeCN)_2.Br_2].Act$.

When $Hg(SeCN)_2$ is dissolved in acetone solutions of $M(NCSe)_2$ (M = Mn or Co), the compounds $M[Hg(SeCn)_2(SCN)_2]$ are formed[124]. The compounds $M[Hg(XCN)A_2]$, where M = Mn, Co, Ni, Zn, or Cu and X = S or Se, have been obtained similarly[123]. Table 5 shows that the spectra of all the compounds of the type $M[Hg(SeCN)_2(SCN)_2]$, where M = Mn, Co, Ni, or Zn, contain high-frequency ν(CN) components in the range 2135–2160 cm^{-1}, which indicates the presence of bridging XCN groups in these compounds. Bridging XCN groups have also been found in $Cu[Hg(SeCN)_2(SCN)_2]$.[123]

When $M(SCN)_2$ (M = Ni, Zn, or Ba) was allowed to react with $Hg(SeCN)_2$ in ethanol or acetone, the compounds $NiHG(SCN)_2(SeCN)_2.Act$, $ZnHg(SCN)_2(SeCN)_2$, and BaHg.

Table 5. Fundamental vibrational frequencies in heteroligand complexes (cm^{-1}).

Compound	SeCN groups			Other acido-groups			Refs.
	ν (CN)	ν (CSe)	δ (SeCN)	ν (CN)	ν (CS)	δ (SCN)	
$[(CH_3)_4N][Au(CN)_2(SeCN)_2]$	2139	533	—	2176	—	—	[119]
$K_2Cd(SeCN)_2(SCN)_2$	2113, 2123, 2135	543, 552	413, 442	2090, 2094	722, 729	438, 444, 458, 473	[120]
$K_2Cd(SeCN)_2Cl_2$	2095, 2110, 2119, 2122	543, 550, 80	403, 402	—	—	—	[120]
$K_2Cd(SeCN)_2Br_2$	2109, 2151	545, 582	404	—	—	—	[120]
$K_4Cd(SeCN)_4(SCN)_2\cdot 0.5Act$	2113, 2122, 2132	540, 551	415, 425	2050, 2091	722, 730, 750	438, 446, 460	[120]
$K_2Cd(SeCN)_3I\cdot Act$	2096, 2112, 2132	534, 632	403	—	—	—	[120]
$K_4Cd(SeCN)_4I_2\cdot 0.5Act$	2074, 2111	540	418	—	—	—	[120]
$[Ph_4P]_2[Cd\{N(CN)_2\}_2(NCSe)_2]$	2080	590	410	2225, 2165	—	—	[121]
$K_4[Cd\{N(CN)_2\}_4(NCSe)_2]$	2105, 2120	—	405	2160	—	—	[121]
$K_2[Cd\{C(CN)_3\}_2(NCSe)_2]$	2125, 2150	590	400	2170, 2220	—	—	[121]
$K_4[Cd\{C(CN)_3\}_2(NCSe)_2]$	2080, 2110	594	415	2180, 2205, 2240	—	—	[121]
$K_2[Hg(SeCN)_2Br_2]$	2125, 2138	531, 539	425	—	—	—	[122]
$K_2[Hg(SeCN)_2I_2]$	2118	546, 621	413	—	—	—	[122]
$K_2[Hg(SeCN)_2(SCN)_2]$	2110	548	424	2110	728	—	[122]
$Ba[Hg(SeCN)_2Br_2]\cdot Act$	2107, 2119, 2138, 2143, 2154	545, 557	410	—	—	—	[122]
$Ba[Hg(SeCN)_2(SCN)_2]$	2120	553, 570	403, 457, 470	2080	747	—	[122]
$Mn[Hg(SeCN)_2(SCN)_2]$	2120, 2135	622	402, 420	2120, 2135	790, 805	—	[123]
$Co[Hg(SeCN)_2(SCN)_2]$	2139, 2146	639	426, 436	2139, 2146	801	—	[123]
$Ni[Hg(SeCN)_2(SCN)_2]$	2160	609	413, 425	2160	768	—	[123]
$Zn[Hg(SeCN)_2(SCN)_2]$	2158	630	404, 420	2158	798, 730	—	[123]
$Cu[Hg(SeCN)_2(SCN)_2]$	2160, 2180	623	405, 427	2160, 2180	760, 830	—	[123]

.$(SCN)_2(SeCN)_2$.Act were obtained[28]. The interaction of $BaBr_2$ with $Hg(SeCN)_2$ in an acetone–water mixture yielded the complex $BaHg(SeCN)_2Br_2$.Act.[28] The compound *trans*-$[(CH_3)_4N][Au(CN)_2(SeCN)_2]$ was isolated from acetone after the double decomposition reaction between KNCSe and *trans*-$[(CH_3)_4N][Au(CN)Cl_2]$.[119] The mixed bismuth complexes $K_3[Bi(SeCN)_3(SCN)_3]$, $K_2[Bi(SeCN)_2(SCN)_3]$, and KBi(SeCN). .$(SCN)_3$ have also been synthesised[125].

When an aqueous solution of $Rh(CH_3COO)_4.2H_2O$ was allowed to interact with potassium selenocyanate, the complex $Rh_2(CH_3COO)_4$.KNCSe.$2H_2O$ was obtained, in which the SeCN groups are of the bridging type[126,127]. A comparative study of the compounds $Rh(RCOO)_2$.KNCSe.$2H_2O$ (R = H, CH_3, CH_2Cl, or C_2H_5) has been made. In these compounds the SeCN groups are of the bridging type and the formula $K[Rh(RCOO)_4NCSe].2H_2O$ can be attributed to the compounds [126]. The beryllium compounds $[Be(DMF)_3Cl]SeCN.3.5DMF$ and $K[Be(DMF)(NCSe)_3].4DMF$ [128] as well as a series of cobalt, manganese, and zinc compounds, namely $K_2[M(NCS)_2(NCSe)_2]$. .*n*Diox (M = Mn, Co, or Zn) and $Na_2[Co(NCSe)_2(NCS)_2]$. .5.5 Diox, in which the SeCN groups are linked to the central atom via nitrogen, have been obtained from non-aqueous solusolutions[129]. Only one absorption band near 16000 cm^{-1}, indicating a tetrahedral environment of the cobalt atom, has been observed in the electronic spectra of the cobalt compounds. The influence of the size of the outer cation on the coordination of the SeCN group was traced in relation to the cobalt selenocyanates $[(C_4H_9)_4N]_3[Co(CN)_5(NCSe)]$, $Cs_3[Co$. .$(CN)_5SeCN]$, $[(CH_3)_4N]_3[Co(CN)_5SeCN]$, $[(CH_3)_4N]_3$.$[Co(CN)_5$. .NCSe], and $[Co(NH_3)_6][Co(CN)_5SeCn]$. The products are $[Co(CN)_5SeCn]^{3-}$ for M = K or Cs, a mixture of $[Co(CN)_5$. .$SeCn]^{3-}$ and $[Co(CN)_5NCSe]^{3-}$ for M = $(CH_3)_4N$, and $[Co(CN)_5NCSe]^{3-}$ for M = $(C_4H_9)_4N$.

The iron(III) complex $[(C_4H_9)_4N]_3[Fe(CN)_5(NCSe)]$ has been isolated from acetone[131]. A series of mixed chromium(III) compounds have been obtained: $[(C_4H_9)_4N]_3[Cr(CN)(NCSe)_5]$, $[(C_4H_9)_4N]_3[Cr(CN)_2.(NCSE)_4]$, $[(C_4H_9)_4N]_3[Cr(CN)_3(NCSe)_3]$, and $[(C_4H_9)_4N]_3[Cr(CN)_4(NCSe)_2]$.[132] The study of the electronic absorption spectra showed that the 18000 cm^{-1} band, due to the *d*–*d* transition, undergoes a hypsochromic shift with decrease of the number of selenocyanato-groups from six to two. The intensity of the charge-transfer bands in the range 28500–30500 cm^{-1} decreases in the same sequence[132].

Polymeric cobalt, nickel, and mercury compounds containing the SCN and SeCN groups have been synthesised[133,134]. The structure of $MHg(SeCN)_4$, where M = Mn or Fe, has been studied[135]. The Co–NCSe–Ag bridging linkages have been detected in $Co[Ag(SeCN)_2]_2$ [136] and the M–NCSe–Hg linkages have been found in $(SeCN)_2L_2M(NCSe)_2Hg(PPh_3)_2$, where M = Co, Ni, Cu, or Zn and L = nicotinamide[137].

VI. COMPOUNDS CONTAINING METAL–PHOSPHORUS AND METAL–CARBON BONDS AS WELL AS CERTAIN OTHER COMPOUNDS

A series of metal complexes of triphenylphosphine (Ph_3P) and triphenylarsine (Ph_3As) have been obtained from non-aqueous solutions. Thus the SeCN groups in *trans*-$Rh(Ph_3P)(CO)NCSe$, $Ir(Ph_3P)_2CO(Act)NCSe$, $Au(Ph_3P)SeCN$, and $Au(Ph_3As)SeCN$ are linked to the rhodium and iridium atoms via nitrogen and to the gold atom via selenium[138]. According to the authors[139], the compound $Pd(Ph_3P)_2(SeCN)_2$ contains Pd–SeCN bonds in the solid state.

The orange crystals of $Ru(CO)(Ph_3P)_2(NCSe)_2$ have been obtained by the reaction of $Ru(CO)_3(Ph_3P)$ with an excess of $(NCSe)_2$ in benzene. A whole series of iridium compounds have been synthesised: $[IrL_2(SeCN)_2]BPh_4$ (where L = Ph_2. .$PC_2H_4PPh_2$), $Ir(Ph_3P)_2(SeCN)_2Cl$, and $Ir(CO)(Ph_3P)_2$. .$Cl(SeCN)_2$.[140] The compounds *trans*-$M(Ph_3P)_2(SeCN)_2$ (M = Pt or Pd) have been obtained by the reaction of equivalent amounts of $(NCSe)_2$ and the corresponding ML_4 in benzene[140]. The NCSe groups in *trans*-$[(Ph_3P)_2PtHSeCN]$ and $\{[(C_4H_9)_4P]_2PtHSeCN\}$ are linked to platinum via the nitrogen atom[141].

The dimer $[(CH_3)_2Au(NCSe)_2]$ with a bridging SeCN group has been obtained; its interaction with triphenylphosphine in absolute ether gives rise to the complex $(CH_3)_2Au(SeCN)$. .(PH_3P), which, however, has not been isolated in a pure state[142]. The compound [MoOClL]Cl, where L = 1,2-bisdiphenylphosphinoethane, has been isolated from a methanol solution[143]. The pentacoordinate complexes CoLNCSe and CoL′(NCSe), which have a trigonal bipyramidal structure, have been obtained by the reaction of COLBr [HL = $P(CH_2$. .$COCH_2R)O(OEt)_2$, R = NEt_2] and [HL′ = $P(CH_2COCH_2R)O$. .$(OEt)_2$, R = $\overline{NCH_2CH_2CH_2CH_2CH_2}$] with KNCSe in dry acetone[144]. The organic ligand is tridentate in both cases; it is coordinated to the cobalt atom via the oxygen of the C=O and P=O groups and via the nitrogen atom, one of the oxygen atoms behaving as a bridging group[144].

The complexes $M(CO)_5(RSeCN)$, where M = chromium or tungsten and R = alkyl or aryl, have also been obtained. The solid compounds are resistant to heat and light. The SeCN group is coordinated to the central atom via the nitrogen atom[145]. The compounds $R_2TlSeCN$ (R = phenyl or *o*-, *m*-, and *p*-tolyl) in which, judging from infrared spectroscopic data, the SeCN groups are linked to thallium via selenium, have been obtained from non-aqueous solutions[146]. The complex $(CH_3)_2N_4BSeCN$ has been synthesised by refluxing $(CH_3)_2NBCl$ with a small excess of AgSeCN in benzene in an atmosphere of nitrogen[147]. The compound [CuLNCSe[.CH_3OH, where L is the macrocyclic ligand 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetra-aza-2,14-dioxacyclotetradeca-3,5,10,12-tetraene has been isolated[148].

The sparingly soluble complexes $Cp_2Ti(NCSe)_2$, Cp_2Ti. .$(CN)(NCSe)$, $Cp_2V(NCSe)_2$, $Cp_2Cr(NCSe)(SCN)$, and Cp_2. .$M(CN)(NCSe)$, where M = V or Cr, have been synthesised by the reaction of $Cp_2Ti(CO)_2$, Cp_2V, and Cp_2Cr (Cp = cyclopentadienyl) with $(SeCN)_2$ and $Se(CN)_2$ in ether in an atmosphere of nitrogen[149].

The synthesis of the compounds $(\eta^5\text{-}C_6H_5)RhL(SeCN)_2$ (R = H or CH_3) has been mentioned[150]. The complexes are obtained by the interaction of $(\eta^5\text{-}C_5R_5)RhLCl_2$ with $NCSe^-$, where L = CNR′ and R′ = C_6H_{11}; the SeCN groups are coordinated to rhodium via selenium.

The synthesis of the compound $CF_3HgSeCN$ has been described[151]. After the reaction of $Cu(SeCN)_2$ with a twofold excess of $CpFeC_5H_4HgCl$, where Cp = $\pi\text{-}C_5H_5$, the complex $CpFeC_5H_4SeCN$ was isolated[152].

An X-ray diffraction study has been made of the compound $KSe(SeCN)_3.0.5H_2O$.[153] The selenotriselenocyanate ions are dimerised to form almost planar groups. All six cyano-groups of the dimeric anion are located on one side of its middle plane. The C≡N (1.21–1.45 Å) and Se–C (1.808 to 1.876 Å) bond lengths have been determined.

The selenotriselenocyanate ions in the rubidium compound $RbSe(SeCN)_3.0.5H_2O$ with an analogous composition are combined into dimers with a similar geometry, which can be regarded as two selenodiselenocyanate molecules linked together via the bridging selenium atoms of two selenocyanate ions. The eight selenium atoms of the dimer are located in approximately the same plane, on one side of which there are six cyano-groups. The coordination of the central selenium atoms is square planar and the four Se–Se

bonds (2.391–2.409 Å) are in the *trans*-positions relative to the four long bonds (3.127–3.331 Å).[154]

The structure of the compound $[(CH_3)_4N][C_6H_5Te(SeCN)_2]$ has also been investigated. It was shown to be isomorphous with the corresponding thiocyanate[155]. The parameters of the monoclinic lattice of the selenocyanate are as follows: $a = 15.840$ Å; $b = 9.341$ Å; $c = 23.384$ Å; $\beta = 100.67°$; $Z = 8$; space group $C2/c$. The coordination of the Te atoms in the anions is of the planar trigonal type due to the phenyl carbon atom. The Se–Te–Se groups are almost linear and the selenocyanate group is linear.

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Thus, since the $SeCN^-$ ions are fairly stable in non-aqueous media, there are considerable prospects for the use of the latter in the synthesis of new compounds incorporating SeCN groups. Further study of compounds of this class will lead to the discovery of their practical applications, for example, in analytical chemistry and in the synthesis of heavy metal selenides and physiologically active preparations[156].

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Plasmo-chemical Reactions of Fluorine and Fluorides

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The reactions of fluorine and its compounds under plasma conditions are discussed. 145 References.

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I. INTRODUCTION

In spite of the very high reactivity of fluorine, reactions involving this element often need to be activated by an electrical discharge or by u.v. radiation. Interest in the reactions of fluorine in discharges was stimulated by recent developments in the synthesis of fine inorganic chemicals, and by the search for new oxidisers and high-energy compounds. The plasmo-chemical synthesis of fluorides is often either the only available method or the most attractive one.

Atomic fluorine, formed by passing molecular fluorine through an electrodeless h.f. discharge (40 MHz, 50 W), has been detected[1] by ESR. A dark red glow discharge, whose spectrum contains strong optical lines from neutral fluorine atoms, develops in a fast flow of the gas at a few hundred Pascal pressure.

Small quantities of atomic fluorine in electrical discharges are usually prepared by using a mixture of fluorine (or volatile fluoride) with an inert gas. For example, the following mixtures have been used: fluorine and argon (0.1–20% F_2),[2-9] fluorine and helium (1–20%),[7,9,10] sulphur hexafluoride and helium[11,12]; atomic fluorine has also been prepared from carbon tetrafluoride[4,13-15]. Power is supplied to the gas reactor from a low-power h.f. or microwave generator, for example a standard microwave generator of frequency 2450 MHz and <200 W output power. The discharge tubes are made of quartz or alumina: the latter is more stable towards atomic fluorine[3-8], but it produces dielectric losses higher than those of quartz tubes. The gas flow emerging from the reactor is used to study the reactions of atomic fluorine (see Ref.16 for a comprehensive review).

The dissociation of fluorine in a microwave discharge can be as high as 60–90%[3,9,10], but the concentration of atomic fluorine in the outlet gas decreases rapidly as a result of recombination and reaction with the wall of the apparatus. The recombination rate constant ($F + F + Ar \rightarrow F_2 + Ar$) is estimated[17] to be $(1.8–6.0) \times 10^{13}$ cm^6 mole^{-2} s^{-1}. A study of the recombination of fluorine atoms in the presence of argon at 295 K and 10–81 mmHg pressure gave an experimental value of $(2.9 \pm 0.2) \times 10^{13}$ cm^6 mole^{-2} s^{-1} for the constant[8]. This value is two orders of magnitude lower than the corresponding rate constants for the recombination of Cl, Br, I, O, and H atoms in argon. Molecular nitrogen (as the third body) is approximately 10 times more effective than argon in bringing about the homogeneous recombination of atomic fluorine[8].

A significant proportion of the fluorine atoms is lost on the apparatus walls. On a quartz surface the loss of F atoms occurs mainly by the reaction with SiO_2, accompanied by the formation of silicon tetrafluoride[4,18,19] and of fluorosiloxane polymers[20]. The probability of disappearance of F atoms as a result of wall collisions has been determined[19,21] for the following surfaces: glass, quartz, mullite–silica, Teflon, copper, stainless steel, nickel, aluminium alloys, and gold.

The formation of fluorine atoms from F_2 molecules in an electrical discharge can take place by different mechanisms: the most probable are described by Eqns.(1) and (2):

$$F_2 + e \rightarrow (F_2^-)^* \rightarrow F + F + e , \quad (1)$$

$$F_2 + e \rightarrow (F_2^-)^* \rightarrow F + F^- . \quad (2)$$

The minimum energy of the colliding electron needed for reaction (1) is 1.5 eV; the dissociative attachment reaction (2) is exothermic, and does not require an activation energy[22]. Reactions (3), (4), and (5)

$$F_2 + e \rightarrow F_2^+ + 2e \quad (3)$$

$$F_2 + e \rightarrow F^+ + F + 2e \quad (4)$$

$$F_2 + e \rightarrow F^+ + F^- + e \quad (5)$$

can take place if the energy of the colliding electrons is not less than 16.6, 19.0, and 15.4 eV respectively[22]. The cross-section of reaction (5) increases monotonically with the electron energy from ~16 to 32 eV: this reaction is predominant for field strengths of ~10^4 V cm^{-1}.[23,24]. The presence of F_2^+ ions in gaseous fluorine passed through a glow discharge (50 mA, 15 kV) has been demonstrated[25] spectroscopically. The reaction $F_2^+ + F^- \rightarrow F + F + F$ is thought to be another probable path for the formation of F atoms[22].

The number of F atoms generated by collisions with electrons is proportional to the energy of the electron beam[22]. The rate of dissociation of F_2 molecules in a glow discharge at 0.5 mmHg pressure increases linearly from 3×10^{16} to 1.2×10^{17} cm^{-3} s^{-1} as the current increases from 4 to 45 mA.[26] The dissociative attachment of electrons to the F_2 molecule has been shown[27,28] to be one of the basic rate-limiting processes in the dissociation of fluorine in the positive column of a glow discharge for currents in the range 0.5–50 mA. The thermal dissociation of fluorine molecules in gas discharge plasmas can be ignored because of the relatively low "molecular" temperature of the plasma[27,29].

From sulphur hexafluoride in a discharge the F atoms are formed mainly by the reaction $SF_6 \rightarrow SF_5 + F$;[30] the dissociation of CF_4 gives not only fluorine atoms and molecules, but also C_2F_6, CF_2, and other fluorinated compounds[4]. Thus, in

spite of their ready availability in a very pure form, SF_6 and CF_4 are not the most convenient sources of fluorine for chemical synthesis in electrical discharges.

Low-frequency glow discharges are used most frequently for the synthesis of fluorides: reactions in electrodeless h.f. and microwave discharges, or in silent (barrier) discharges, have not been studied in detail. Whenever possible, the prepared mixture of fluorine (or volatile fluoride) and the other reactant is introduced into the discharge reactor, or the reactants are condensed on the reactor wall and exposed to fluorine (or a fluoride) which has been activated in the discharge. Reactions involving fluorine or a fluoride are usually carried out in reactors cooled to very low temperatures. Often a valuable product can be synthesised only if the reactor walls are cooled in liquid nitrogen, but this is easily done because the discharge current is usually 20–50 mA, corresponding to a power dissipation of only 100–150 W.

In the following Sections we shall review experimental data on the reactions of fluorine and fluorides in an electrical discharge reported since 1969–1970, and therefore not included in earlier reviews[31,32]. Some older work not mentioned in those reviews will also be discussed here.

II. SYNTHESIS OF THE NITROGEN FLUORIDES, TRIFLUORAMINE OXIDE, AND TETRAFLUORO-AMMONIUM SALTS

1. Synthesis of Nitrogen Trifluoride

Nitrogen fluorides have a variety of applications in the synthesis of fine inorganic chemicals and in preparative organic chemistry[33]. In the absence of external agencies such as electrical discharges or ionising radiation fluorine does not react with nitrogen. The nitrogen fluorides NF_3, N_2F_4, N_2F_2, and N_3F are therefore usually prepared from compounds containing bound nitrogen. However, the synthesis of nitrogen trifluoride from the elements is thought[34] to be thermodynamically possible at temperatures below ~900 K. A calculation[35] of the equilibrium composition of the nitrogen–fluorine system shows that at 200–1000 K, for total pressures of 20 or 760 mmHg, and for atomic ratios F : N = 1 : 3, 1 : 1, or 3 : 1 the main fluorine-nitrogen component of the system at equilibrium is nitrogen trifluoride[36], whose concentration is a maximum and close to 1 (in mole fraction) at 200–600 K. As the temperature increases to 700–1000 K the concentration of NF_3 decreases as a result of dissociation, and at 1500 K it becomes negligibly small[37].

The preparation of NF_3 in 30% yield from the elements in a glow discharge was reported[38] in 1964, but the synthesis of NF_3 in a glow discharge appears[39] to have first achieved in 1960. The synthesis of nitrogen trifluoride is possible whether or not the discharge tube is cooled in liquid nitrogen: if all other conditions are the same, a better yield is obtained by using cooled U-tubes for the reaction. The electrodes can be made of copper, nickel, copper–nickel alloy, or steel, since none of these materials has a significant influence on the yield of NF_3. Electrodes made of silver or silver–copper alloy disintegrate rapidly in an atmosphere of fluorine, but they give a higher yield of NF_3 than (say) copper electrodes[40]. Varying the fluorine to nitrogen ratio in the initial mixture of gases does not lead to the synthesis of additional products (other than nitrogen trifluoride). The yield of NF_3 is almost independent of the composition of the initial mixture, and increases with the energy dissipated per unit volume of reacting gases to a maximum of 60–70%.[31] Because of its high energy consumption the plasmo-chemical method of synthesis of NF_3 has only limited preparative value. Fluorination of $^{15}N_2$ in a glow discharge has been used[41] to prepare $^{15}NF_3$. Nitrogen trifluoride has been synthesised from the elements also in a barrier discharge (though in low yield)[42], and in a pulsed u.h.f. discharge[43].

2. Dissociation of Nitrogen Trifluoride

Nitrogen trifluoride is unstable in electrical discharges, and easily dissociates into fluorine and nitrogen[31]. The dissociation is reversible, and if the flow rate of the NF_3 through the reactor is slow a limiting concentration of the dissociation products is observed, which depends (among other things) on the strength of the discharge current. For example, for a pressure of 15 mmHg in the glow discharge the degree of dissociation is 70, 90, and 96% for discharge currents of 12, 25, and 40 mA respectively[44]. The limiting degree of dissociation of NF_3 in a barrier discharge under circulating flow conditions[42] is 98%; almost complete decomposition of the NF_3 is obtained also in a u.h.f. discharge[43].

The effect of added fluorine, nitrogen, and oxygen on the decomposition of NF_3 has been studied[45] in a glow discharge without cooling the walls of the reactor in liquid nitrogen. Fluorine inhibits the decomposition slightly, probably by displacing the reaction $NF_3 \rightleftharpoons F + NF_2 \rightleftharpoons 2F + NF \rightleftharpoons 3/2F_2 + 1/2N_2$ towards the regeneration of nitrogen trifluoride. Addition of nitrogen accelerates the decomposition of nitrogen trifluoride, possibly by transfer to the NF_3 molecules of the energy of the electronically excited N_2 molecules: it is well known[46] that NF_3 can be decomposed by active nitrogen, though less readily than ammonia. Addition of oxygen also accelerates the decomposition of NF_3. Under these conditions the system contains fluorine, nitrogen, NO_2, and (in some experiments) N_2O_5. The reason for the absence of nitryl fluoride is not clear, since mixtures of NO_2 and fluorine are known[47] to give FNO_2 very readily by the reactions

$$NO_2 + F_2 \rightarrow FNO_2 + F, \quad NO_2 + F + M \rightarrow FNO_2 + M.$$

The tendency of nitrogen trifluoride to dissociate in a discharge allows this material to be used as a fluorinating agent. Thus, a mixture of NF_3 and O_2 in a tube cooled in liquid nitrogen gave oxygen fluorides at a current of 20 mA and 0.6 mmHg pressure[48], though the formation of trifluoramine oxide (F_3NO) was not detected. Yet, this compound was later synthesised by exactly the same reaction (NF_3 and O_2 in a discharge tube at 77 K: see, for example, Ref. 49). The action of a glow discharge on a mixture of bromine and NF_3 produces bromine fluorides[50]. Bromodifluoramine $BrNF_2$, a possible product of the reaction between Br atoms and NF_2 radicals, is not formed in a glow discharge. The NF_2 radicals formed by the decomposition of NF_3 may be in an unstable excited state which rapidly breaks down. The reaction between NF_3 and chlorine in a microwave discharge gave ClF and nitrogen, but not $ClNF_2$ or Cl_2NF.[51]

3. Synthesis of Difluorodiazine and Tetrafluorohydrazine

Difluorodiazine N_2F_2, which can exist as *cis*- and *trans*-isomers, is formed in trace quantities during the synthesis of NF_3 from the elements in a barrier discharge. Tetrafluorohydrazine (N_2F_4) also could not be obtained in reasonable yield, either from fluorine and nitrogen or from the decomposition of nitrogen trifluoride. One of the factors opposing the synthesis of N_2F_2 and N_2F_4 in discharges is the instability of these compounds in the presence of fluorine,

with which they react to give nitrogen trifluoride. Difluorodiazine N_2F_2 frozen on the wall of the discharge tube at 77 K rapidly reacts with fluorine in a glow discharge to give NF_3. The reaction between N_2F_4 and OF_2 in a discharge at 77 K gives NF_3, NOF, and NO_2F.[39] N_2F_2 and N_2F_4 can be prepared from nitrogen trifluoride in a discharge tube if a fluorine acceptor (for example, mercury) is added[31,52].

4. Synthesis of Trifluoramine Oxide

The synthesis of trifluoramine oxide F_3NO was reported[53-55] in 1966, though there is evidence in the Patent literature that the compound has been known in some laboratories since 1961 to 1962. F_3NO can be synthesised by plasmo-chemical and photochemical methods as well as by methods not involving radiation or low-temperature plasmas.

Different combinations of the basic components (nitrogen, oxygen, and fluorine) can be used for the synthesis of F_3NO in electrical discharges: $N_2+O_2+F_2$,[56] $N_2+OF_2+F_2$,[57] NF_3+OF_2,[57-60] NF_3+O_2,[49,55,61,62] NF_3+N_2O,[61] and NO_2+F_2.[56] A calculation[36,63] based on published thermodynamic data[35] shows that the N + O + F system at equilibrium may contain substantial amounts of F_3NO, the shape of the equilibrium diagram being very dependent on the N : O : F ratio. The mole fraction of F_3NO in the system at equilibrium is relatively high only at 200–300 K, and falls off very steeply at higher temperatures. Since F_3NO is stable at low temperatures it is essential to quench the products at the conclusion of the plasmo-chemical preparation of this compound. The synthesis of F_3NO in a glow discharge is carried out in tubes cooled to 77 K by immersing the reaction volume either wholly or partly in liquid nitrogen. Attempts to "extract" the F_3NO from the discharge and to condense it in a remote trap were unsuccessful.

The yield of F_3NO from nitrogen trifluoride and oxygen[49,55,62,64] is 10–15%, with ~70% utilisation of the NF_3. In addition to F_3NO the reaction produces oxygen fluorides, oxides of nitrogen, and ozone. Ozone formation can be suppressed by using an excess of NF_3 (for example, by using $NF_3 : O_2$ ratios between 2 : 1 and 6 : 1 in the initial mixture[62]). The synthesis of F_3NO from mixtures of NF_3 and OF_2 does not differ in principle from the synthesis from NF_3 and O_2, since the OF_2 merely acts as a source of oxygen by decomposing into its elements in the discharge. Trifluoramine oxide has been prepared in 20–40% yield from an $NF_3 : OF_2 : Ar = 1 : 1 : 2$ mixture[65].

Mixtures of fluorine, nitrogen, and oxygen are not a very convenient reagent for the preparation of F_3NO in spite of the ready availability of the starting materials. When these mixtures are used the formation of F_3NO is suppressed by a competing reaction: the formation of O_2F_2, which consumes 94 to 97% of the oxygen reaching the discharge (assuming an $F_2 : N_2 : O_2$ ratio of 3 : 1 : 1 in the initial gas mixture)[64,66]. The yield of F_3NO cannot be improved by adding an excess of oxygen: this could merely convert the whole of the fluorine present in the system into O_2F_2.

The reaction between fluorine and nitrous oxide has been studied in detail[66]. The extent of conversion of N_2O into F_3NO, calculated by the equation $N_2O + 3/2F_2 = F_3NO + 1/2N_2$, is almost independent of the composition of the mixture, and goes through a maximum (~20–22%) as the flow rate of the gas is increased. Up to 40–50% of the oxygen formed by the dissociation of N_2O reacts with the fluorine to give O_2F_2: ozone formation is negligible, making this method of synthesis safer than the preparation of F_3NO from NF_3 and O_2. In the absence of an electrical discharge the reaction between fluorine and nitrous oxide at 573–1073 K produces a mixture of FNO and NF_3.[67]

Trifluoramine oxide has been obtained in small amounts (0.5 mmole h^{-1}) from a mixture of N_2, O_2, and F_2 (1 : 1 : 3) in a microwave discharge at a pressure of ~0.5 mmHg.[68] The low yield of F_3NO is probably due to the low power of the microwave source used, which prevented the use of higher pressures. Another possible reason for the low yield is the difficulty of synthesising F_3NO from the elements, which was mentioned above.

Thus the plasmo-chemical synthesis of F_3NO is fairly laborious, offers only a moderate yield, and is accompanied by the formation of large amounts of side products. The photochemical method of preparing F_3NO[69-71] is similar in many ways to the plasmo-chemical methods and has an even lower yield. The most promising method appears to be the combustion of nitric oxide in fluorine in a flow reactor[72]. All methods of synthesis of F_3NO apparently include the following main steps: 1) formation of nitric oxide, 2) fluorination of nitric oxide in nitrosyl fluoride [$NO + F(F_2) \rightarrow NOF(+F)$], 3) fluorination of the nitrosyl fluoride ($NOF + 2F \rightarrow F_3NO$). The nitric oxide may be introduced as a reactant or formed in the plasma (by the oxidation of nitrogen or by the decomposition of nitrous oxide).

5. Synthesis of Tetrafluoro-ammonium Salts

Even quite recently the synthesis of stable tetrafluoroammonium salts was believed to be impossible. According to Wilson[73], only $NF_4^+BF_4^-$ could have enough thermal stability to exist as a stable compound at temperatures below 153 K. However, two papers[74,75] published in 1966 reported the preparation of the salts $NF_4^+AsF_6^-$ and $NF_4^+SbF_6^-$, which are stable at room temperature but rapidly decompose at temperatures above 543–573 K. In 1970 the compound $NF_4^+BF_4^-$ was synthesised[76], and found to be stable up to 513–623 K. In recent years a few more salts containing the NF_4^+ cations have been prepared. The tetrafluoro-ammonium compounds are powerful oxidising agents: they can be used, in principle, as components of solid rocket fuels[77], in gas generating apparatus[78,79], and in laser technology[80,81]. Tetrafluoroammonium hexafluoro-arsenate and tetrafluoroborate have been synthesised in a glow discharge.

The compound NF_4AsF_6 was prepared by circulating a mixture of NF_3, AsF_5, and F_2 (1 : 1 : 2) in a glow discharge apparatus with a discharge tube cooled to 195 K.[31,75,82,83] In very long (~40 h) experiments with inadequate cooling the reactor wall suffered serious corrosion, forming salts with oxygenated cations which contaminated the desired product. In an experiment[84] with a high-pressure mercury lamp irradiating an equimolar mixture of NF_3, AsF_5, and F_2 in a quartz vessel at room temperature the compound $O_2^+AsF_6^-$ was obtained instead of NF_4AsF_6 as a result of corrosion of the walls of the vessel. At 77 K the same reactants in a quartz reactor irradiated with light from a 900 W mercury lamp yielded NF_4AsF_6 at a rate greater than 1 g h^{-1}.[81]

Attempts to synthesise NF_4BF_4 in a glow discharge with a reactor cooled to 195 K proved unsuccessful[85,86]: instead of NF_4BF_4, $O_2^+BF_4^-$ was obtained together with a salt which hydrolysed to give nitrogen oxides. In order to obtain NF_4BF_4 from NF_3, BF_3, and fluorine the reactor walls must be cooled in liquid nitrogen[76,87-89]. The synthesis is carried out as follows: the NF_3 and BF_3 are condensed on the wall of a U-shaped discharge tube, and gaseous fluorine is slowly allowed to flow through the discharge at 30–55 mmHg with a current of 30 mA. After 1 h of discharge a fluorine flow of 400 cm^3 h^{-1} produces ~3 g of NF_4BF_4 in a yield approaching 100%. Up to 3 g h^{-1} of NF_4BF_4 can be obtained by an improved variant of the photochemical method

of synthesis from NF_3, BF_3, and F_2 at 77 K in a reactor made of steel and sapphire[81].

Reactions in which NF_3^+ or F^+ ions give NF_4^+ (for example, $NF_3^+ + F \rightarrow NF_4^+$, or $NF_3 + F^+ \rightarrow NF_4^+$) are possible, in principle, in an electrical discharge, but not in the photochemical or thermal synthesis of tetrafluoro-ammonium salts, since the u.v. energy or the thermal energy of the reactants at 373 to 473 K is insufficient to ionise NF_3 or F. In this context it is interesting to consider the suggestion[84] that the active particles responsible for the oxidation of NF_3 could be the radicals $AsF_6^{\cdot}$, which have a high electron affinity and are formed from a fluorine atom and a molecule of the Lewis acid AsF_5. The reaction between $AsF_6^{\cdot}$ and NF_3 would give first $NF_3^+AsF_6^-$ and then $NF_4^+AsF_6^-$ (by the addition of a fluorine atom).

The possible existence of the radicals $AsF_6^{\cdot}$, $SbF_6^{\cdot}$, $Sb_2F_{11}^{\cdot}$, and the cation radical $NF_3^{\cdot+}$ was confirmed experimentally[90] by γ-radiolysis of the salts NF_4AsF_6 and $NF_4SbF_6.0.8SbF_5$ at 77 K. It was also shown that $NF_3^{\cdot+}$ can be formed as an intermediate during the photochemical synthesis of NF_4AsF_6 and NF_4BF_4 from mixtures of NF_3, F_2, and a Lewis acid[91]. The radical $BF_4^{\cdot}$ was not detected during the radiolysis of NF_4BF_4, possibly because of its low thermal stability. The instability of $BF_4^{\cdot}$ may also explain the failure to obtain NF_4BF_4 in a glow discharge at 195 K.[85,86]. A study[92] of the thermal decomposition of the salts NF_4BF_4 and NF_4AsF_6 finally led to the rejection of the mechanism of formation of NF_4^+ through the formation of radicals of the $AsF_6^{\cdot}$ type and their reaction with NF_3 molecules, and to its replacement by the mechanism

$$F_2 \rightleftarrows 2F, \quad F + NF_3 \rightleftarrows NF_4,$$
$$NF_4 + AsF_5 \rightleftarrows NF_3^+AsF_6^-, \quad NF_3^+AsF_6^- + F \rightleftarrows NF_4^+AsF_6^- .$$

III. SYNTHESIS OF OXYGEN FLUORIDES

The reaction between fluorine and oxygen and the synthesis of oxygen fluorides in a glow discharge are discussed in earlier reviews[31,32]. The plasmo-chemical method was, for a long time, the only method of preparing the compound dioxydifluoride O_2F_2. In 1969 a radiation-chemical synthesis of O_2F_2 was reported[32], and more recently it was suggested that the compound can be obtained by irradiating a mixture of $O_2 + F_2$ or $OF_2 + F_2$ at 77 K with light from a mercury lamp (365 nm)[93] or by fluorinating the oxygen with thermocatalytically generated atomic fluorine[94].

The reality of the existence of higher members of the polyoxydifluoride series O_nF_2 ($n = 2$–6) had been questioned (see previous reviews[31,32]). Pshezhetskii and coworkers[95] doubt the existence of tetraoxydifluoride O_4F_2 as a pure compound. The electronic absorption spectrum of the product obtained by a method[96] claimed to give O_4F_2 in a glow discharge was assigned to a mixture of O_2F_2 and the radicals $O_2F^{\cdot}$. The compound of empirical formula O_4F_2 is thought[95] to be the radical $O_2F^{\cdot}$, at least in dilute solutions (in liquid argon, oxygen, or CF_4). The reaction between fluorine and oxygen in a glow discharge with reactor walls cooled to 77 K or below apparently gives only one of the "polyoxydifluorides": the dioxydifluoride, which may contain the $O_2F^{\cdot}$ radical in concentrations anomalously high for a free radical.

The action of a barrier discharge on a fluorine–oxygen mixture has been studied[97,98]. Pyrex glass ozonisers made of three coaxial tubes were used as reactors. Power was supplied to the ozonisers from an audio-frequency signal generator and amplifier; the reaction was studied in a circulating regime with the fluorine–oxygen mixture at an initial pressure of 100–600 mmHg. The ozoniser wall was cooled in running water, and the gas flow from the ozoniser was led by a connecting tube to a trap cooled in liquid nitrogen ~50 cm away from the ozoniser. A yellow or orange solid was condensed in the cold trap, though in some experiments the condensate (at 77 K) contained a dark red liquid. The composition of the low-temperature condensate obtained from an ozoniser in which the discharge gap was 1 mm wide varied according to the composition of the initial gas mixture, the power of the discharge, the time for which the gas was circulated, and the initial pressure of the gas. The O : F atomic ratio in the condensate varied between 1.1 and 2.04. The most probable combination of oxygen fluorides (to account for a chemical analysis of $O:F = 1.1$–2.04) is the mixture $O_2F_2 + (O_2F)_x$ (mistaken for "O_4F_2" when $x = 2$). The oxygen content in the condensate tends to increase with the circulation time of the initial gas mixture and with its oxygen content, and with a decrease in the power of the discharge and in the initial pressure in the reactor. On heating the tube connecting the ozoniser to the cold trap from room temperature to 323–333 K the rate of formation of condensate in the trap falls off very steeply, though some condensation persists even under conditions clearly unsuitable for the transport of "cryogenic" compounds. The O : F ratio in the condensate remains close to 2 under these conditions, i.e. the condensate approaches the composition "O_4F_2" corresponding in reality to any agglomerate of the $(O_2F)_x$ type.

Since O_2F_2 is thermally more stable[31] than "O_4F_2" the enrichment of the condensate in the "tetra-oxydifluoride" on heating the connecting tube is unexpected. Evidently, the $O_2F^{\cdot}$ radicals are more stable than the O_2F_2 molecules, and these molecules are decomposed preferentially in the heated gas stream, leading to a change in the $O_2F_2 : O_2F^{\cdot}$ ratio in favour of the $O_2F^{\cdot}$ radicals and to a corresponding change in the composition of the condensate. The $O_2F^{\cdot}$ radicals are stable towards F_2 molecules, and they are fluorinated to O_2F_2 only under the influence of atomic fluorine. The compound dioxygenyl hexafluoroarsenate $O_2^+AsF_6^-$, which dissociates on heating with evolution of $O_2F^{\cdot}$,[99] has been used recently to prepare $O_2F^{\cdot}$ radicals and to study their properties.

The condensate obtained from an ozoniser with a discharge gap 0.5 mm wide contains, in addition to the unstable oxygen fluorides, the stable compound oxygen difluoride[98]. The synthesis of $OF_2^{\cdot}$ is very slow: under the most favourable experimental conditions the yield of $OF_2^{\cdot}$ was only 2 mmole h^{-1}. The low rate of formation of $OF_2^{\cdot}$ is explained by the presence of a competing reaction (the synthesis of the unstable oxygen fluorides) and by the difficulty of stabilising the oxygen difluoride in the discharge apparatus of the chosen type.

As a method of synthesis of oxygen fluorides the barrier discharge is inferior to the glow discharge not only in terms of apparatus complexity and of yield, but also because the composition of the condensate is more sensitive to experimental conditions.

IV. SYNTHESIS OF THE HALOGEN FLUORIDES AND OF CHLORINE OXYTRIFLUORIDE

The compounds of fluorine with chlorine, bromine, or iodine are prepared from the elements at room temperature or with moderate heating[100]; many methods of preparing chlorine oxide fluorides are also known. Electric discharges

have been used in the search for methods of synthesis of higher halogen fluorides and of new chlorine oxyfluorides.

1. Synthesis of Chlorine Pentafluoride

An unsuccessful attempt to prepare ClF_5 from ClF_3 and fluorine in an electrical discharge was reported[39] in 1957. The first disclosure[101] of the synthesis of chlorine pentafluoride at elevated temperature and pressure was in 1963; a patent application for the preparation of ClF_5 in a discharge[102] appeared in the same year. In the glow-discharge synthesis[102,103] a mixture of fluorine and chlorine is passed through a U-shaped discharge tube with copper electrodes (cooled to 195 K), and the gases from the outlet are taken to a trap at 77 K. The pressure (30 mmHg) and current (30 mA) in the discharge are kept constant. The reaction products (ClF, ClF_3, and ClF_5) can be separated by low-temperature sublimation. Fluorine can be made to react with chlorine both in a glow discharge (with direct current or at mains frequency) or in an h.f. discharge[102]. Instead of fluorine and chlorine, binary compounds of fluorine and chlorine can be used[102] for the synthesis of ClF_5 (ClF, ClF_3, NF_3, N_2F_2, N_2F_4, NCl_3) as long as the number of fluorine atoms in the initial mixture is in 1–10 fold stoichiometric excess over the number needed to form ClF_5.

The salt $ClF_6^+PtF_6^-$, whose cation can be formally considered to have been derived from the hypothetical chlorine fluoride ClF_7, has been described (see, for example, Ref.104). It was synthesised by photochemical oxidation of ClF_5, using PtF_6, but attempts to produce ClF_6^+ in a glow discharge were unsuccessful[104]. A glow discharge in a reactor made of Pyrex glass, at 195 K and 20–50 mmHg pressure, yields $ClF_2^+BF_4^-$ (but not $ClF_6^+BF_4^-$) from a mixture of $BF_3 + F_2 + ClF_5$ (1:1 and 42:1). Obviously, the ClF_5 dissociates with formation of ClF_3, which reacts with the BF_3 present in the system to give crystalline $ClF_2^+BF_4^-$.[104,105]

2. Synthesis of Bromine Pentafluoride

The reaction between bromine and fluorine in a glow discharge is carried out by freezing bromine in a U-shaped discharge tube at 195 K and adding fluorine to the discharge, either continuously or in portions, while maintaining a pressure of 20–25 mmHg and a discharge current of 20–30 mA.[50] As the reaction proceeds the deeply coloured bromine is converted into the colourless bromine pentafluoride. An 80 to 85% extent of conversion of the Br_2 (calculated as BrF_5) is reached in a few minutes, but the reaction then slows down, and quite long times are needed for the reaction to go to completion. The final yield of BrF_5 is almost 100%. Cooling the walls of the discharge tube with liquid nitrogen lowers the rate of fluorination very strongly, probably by suppressing the renewal of the frozen bromine surface and thus making the underlying layers of condensate inaccessible to the fluorine. The reaction between fluorine atoms and bromine molecules also gives bromine pentafluoride[9].

Unsuccessful attempts have been made to prepare bromine heptafluoride[106]: apparently, BrF_7 (like ClF_7) is unstable towards dissociation into the pentafluoride and fluorine, even at very low temperatures. However, the salts $BrF_6^+AsF_6^-$ and $BrF_6^+Sb_2F_{11}^-$, which contain the BrF_6^+ cation, are known[106]. They are prepared by oxidising bromine pentafluoride with $Kr_2F_3^+$ or KrF^+. The resulting BrF_6^+ is one of the strongest oxidising agents known, and it can easily oxidise O_2 to O_2^+ or xenon to XeF^+ under normal conditions.

3. Synthesis of Chlorine Oxytrifluoride

Chlorine oxytrifluoride F_3ClO was first synthesised in 1965 by a group of workers in the USA,[107] and the synthesis was later confirmed by an independent group in France[108] in 1970. Several methods of preparing F_3ClO have since been reported (see, for example, Ref.109), but they all have serious drawbacks: they are laborious, the reactants are not easily available, the yield of product is low, etc.

Chlorine oxytrifluoride, like trifluoramine oxide, can be prepared in an electrical discharge. In addition to their formal similarity, the reactions leading to the synthesis of F_3ClO and F_3NO have one important feature in common: the need to stabilise the end product very effectively. The quenching and storage of F_3ClO is complicated by the very high reactivity of this compound, which attacks glass or quartz even at temperatures below 273 K. The synthesis of F_3ClO in an electrical discharge has not been studied fully. The compound was first prepared[107] by freezing Cl_2O at 77 K on a Pyrex glass U-tube reactor and passing fluorine at 20 mmHg pressure through the discharge. The products contained ClF_5 (~45 mole %), $FClO_2$, ClF_3, and only 1–2% of F_3ClO. The formation of F_3ClO from ClF_5 and O_2 in a glow discharge with reactor walls cooled to 77 K has been reported[105]. If the wall temperature is raised to 195 K, a strong acceptor of fluoride ions (like BF_3) is needed to fix the F_3ClO in the form of the salt $F_2ClO^+BF_4^-$. Low-temperature fluorination of the salt $ClO_2^+BF_4^-$ in a glow discharge also gives $F_2ClO^+BF_4^-$.[110] Chlorine oxytrifluoride is one of the products of the reaction of perchloryl fluoride $FClO_3$ with fluorine in a glow discharge at 77 K.[105] The action of a glow discharge on a mixture of F_2, Cl_2, and O_2 yields chlorine oxytrifluoride, but in a yield not exceeding 6%.[105] Similarly low yields were reported (see above) for the preparation of trifluoramine oxide from its elements.

V. SYNTHESIS OF THE INERT GAS FLUORIDES

Early work on the synthesis of krypton and xenon fluorides is reviewed in Ref.31. The most difficult to prepare is krypton difluoride, due to the low reactivity of krypton and the low thermal stability of KrF_2. Yields of ~1 g h^{-1} were obtained[111] in the synthesis of KrF_2 in a glow discharge at a current of 10 mA. When the reactor is at 123 K krypton difluoride is not formed. The use of a barrier discharge in a reactor cooled in liquid oxygen or nitrogen gave a yield[112] of KrF_2 of 50 mg kW^{-1} h^{-1}. In a photochemical method[113] of preparing KrF_2 by irradiating a mixture of krypton and fluorine (condensed at 77 K) with light from a mercury lamp the yield of KrF_2 was 4.7 g after 48 h. The photochemistry of krypton difluoride was studied also by Legasov and coworkers[114–116]. KrF_2 is produced at rates of up to 6 kg h^{-1} by treating krypton frozen at 77 K with atomic fluorine generated by a heated nickel catalyst[117]. The reaction between krypton and fluorine in a glow discharge in the presence of antimony pentafluoride[118] gave $KrF^+SbF_6^-$ if the reactor walls were cooled with liquid nitrogen and the discharge current was 10–30 mA.

Xenon difluoride has been prepared in almost 100% yield from a mixture of fluorine and xenon in a glow discharge at 196 K.[119] In the presence of an excess of fluorine XeF_4 is formed, but the tetrafluoride cannot be prepared free from traces of XeF_2 in a glow discharge. A mixture of fluorine and xenon (3:1) was shown[120] to yield XeF_2 contaminated with $XeF_2.XeF_4$ in the early stages of the reaction, and XeF_6 containing a small amount of $XeF_2.XeF_4$ in the later stages. The absence of XeF_4 crystals at all stages of the reaction

was demonstrated by X-ray phase analysis. The authors conclude[120] that the xenon fluorides are formed by the successive fluorination of XeF_2 to XeF_4, and XeF_4 to XeF_6, at rates one order of magnitude lower for each step.

XeF_4 has been synthesised (in yields of up to 39.3 g h^{-1}) by treating solid xenon in a "fluidised" bed with atomic fluorine generated in an h.f. discharge (8 MHz, 0.1–2 kW).[29] Xenon difluoride has been prepared in a pulsed high-pressure discharge with a current of amplitude 50 kA and frequency 70 kHz.[121] The photochemical reaction of xenon with an excess of fluorine ($Xe:F_2 = 1:4–6$) yields XeF_4 at room temperature[122]; the reaction takes place in two steps, and the fluorination of XeF_2 to XeF_4 is ~20 times slower than the fluorination of Xe to XeF_2. The interaction of F atoms with XeF_2 or XeF_4 was not detected in a kinetic study[9] of the reactions of atomic fluorine: the reason is not clear.

Xenon dichloride for spectroscopic work has been prepared by condensing on a cold surface (10–15 K) a mixture of xenon and chlorine which had passed through a microwave discharge[123].

VI. OTHER REACTIONS OF FLUORINE AND FLUORIDES

Many element–organic compounds containing trifluoromethyl groups can be synthesised by using an h.f. discharge: HgR_2, $RHgX$, R_2Te_2, R_2Te, SnR_4, GeR_4, BiR_3 (where $R = CF_3$, $X = Cl$, Br, I).[124–126] The $CF_3^{\cdot}$ radicals are obtained by the dissociation of hexafluoroethane in an h.f. discharge (8.6 to 13.6 MHz) at 0.5–2 mmHg pressure. The course of the reaction is strongly influenced by the power dissipated in the discharge. The dissociation of C_2F_6 into $CF_3^{\cdot}$ radicals requires only 20–25 W, and the use of higher powers causes more substantial decomposition of the C_2F_6 molecule with formation of fluorine atoms and $CF_2^{\cdot}$ radicals. The C–C bond is much less stable than the C–F bond in the C_2F_6 molecule, and the power of the discharge is used initially in breaking the C–C bonds, thus allowing C_2F_6 to be used as a source of pure $CF_3^{\cdot}$ radicals. These radicals can react with the halides of mercury, tellurium, tin, etc. to give the corresponding element–organic compounds. The reactions are slow: typical rates for the synthesis of HgR_2, SnR_4, and BiR_3 are 8, 1, and 0.2 g day^{-1} respectively. The unstable compound $Xe(CF_3)_2$ has been obtained[127] by the reaction of XeF_2 with $CF_3^{\cdot}$ radicals generated from C_2F_6 in the plasma of an h.f. discharge.

Hexafluoro-acetone is an alternative source of CF_3 radicals in an h.f. discharge. The concentration of $CF_3^{\cdot}$ radicals increases linearly with the function $W(P/P_0)^{1/2}$, where W is the power of the discharge (3–24 W), P is the partial pressure of $(CF_3)_2CO$ (0.016–0.064 mmHg), and P_0 is the pressure of the mixture of $(CF_3)_2CO$ and the argon diluent (0.4 to 0.9 mmHg).[128] On the assumption that the $CF_3^{\cdot}$ radicals disappear only by homogeneous recombination the rate constant of the radical formation reaction $(CF_3)_2CO \rightarrow 2CF_3^{\cdot} + CO$ is proportional to the square of the power. Hexafluoro-acetone in an h.f. discharge also acts as a source of the relatively long-lived difluoromethylene radicals (also obtained from CF_4 in a glow discharge and from perfluorocyclobutane in an h.f. discharge)[129]. The $CF_2^{\cdot}$ radicals play an important role in the decomposition of polytetrafluoroethylene in a microwave discharge[130]. In a glow discharge with the reactor cooled to 77 K the compound tris(trifluoromethyl)-hydroxylamine $(CF_3)_2NOCF_3$ yields both $CF_3^{\cdot}$ radicals and fluorine atoms, forming CF_4, COF_2, CF_3NCF_2, C_2F_6, $(CF_3)_2NF$, and $(CF_3)_3N$.[131] The application of a barrier discharge to CF_3PH_2 produces perfluorohydrocarbons, and also the trifluoromethylphosphines $(CF_3)_2PH$, $(CF_3)_3P$, and $CF_3PHPHCF_3$; from $(CF_3)_2PH$ the compounds CF_3PH_2, $(CF_3)_3P$, and $(CF_3)_4P_2$ have been obtained[132].

Polymeric carbon monofluoride $(CF_x)_n$ can be prepared by the reaction between powdered graphite and a fluorine plasma[133,134]. The reaction is carried out in a pseudo-condensed layer at a pressure of 2–5 mmHg. A stream of fluorine passes through the h.f. discharge (20 MHz, 480 W) and reacts slowly with the powdered graphite, giving a snow-white polymeric powder of composition $CF_{1.19}$. A substance of composition $CF_{0.68}$ is also formed, as well as the volatile side-product CF_4. The $(CF_x)_n$ product is almost black for $x = 0.68–0.8$, grey for $x = 0.8–0.95$, and white for $x = 0.95–1.12$. White samples are stable in air at up to ~873 K. Polymeric carbon monofluoride can be used as a high-temperature lubricant in oxidising atmospheres and for frictional components carrying a high load; another potential application of this compound is as a cathode material for high-capacity accumulators.

The silicon analogue of the carbene (SiF_2) is formed in small amounts during the dissociation of silicon tetrafluoride in a glow discharge[135]. Linear and cyclic fluorosiloxanes have been detected mass-spectrometrically[136] among the products of a microwave discharge in SiF_4. A fluorosiloxane polymer of composition $(SiO_{1.5}F)_n$ was obtained from the reaction of SiF_4 with oxygen in a microwave discharge[20]. Trifluorosilane decomposes in a glow discharge, giving SiF_4, Si_2F_6, and a polymeric compound[137].

Sulphur tetrafluoride gives SF_6 in 80% yield in the plasma of a microwave discharge[138]. Sulphur hexafluoride is formed also by the decomposition of S_2F_{10}, SF_5Cl, or $(SF_5)_2O_2$ in a microwave discharge, and the reactions of SF_6, SF_2F_{10}, or SF_4 with chlorine give SF_5Cl.[139] Passing a mixture of selenium hexafluoride and chlorine through a u.h.f. discharge gives only SeF_4.[139] The plasmo-chemical decomposition of SF_6 in a quartz reactor can yield sulphur oxide fluorides formed by the attack on the reactor walls. Thus, substantial amounts of SOF_4, SO_2F_2. SOF_2, and also SiF_4 have been obtained[140] during the decomposition of SF_6 in a quartz reactor by h.f. discharge. A mass spectrometric study of the interaction of SF_6 with the nitrogen plasma of an h.f. discharge revealed the presence of SF_2 as one of the main components of this plasma system, whereas nitrogen fluorides were formed only in trace amounts[141]; the reaction of SF_6 with an oxygen plasma gave OF_2, SO_2, and SOF_2.

Sulphur hexafluoride or a mixture of SF_6 with oxygen, and also carbon tetrafluoride and other fluorocarbons, have been used as the plasma-forming gases in the plasmo-chemical etching of Si, SiO_2, and photoresist in integrated circuit technology (see, for example, Ref. 142). Both fluorine atoms and fluorine molecules, produced by the decomposition of the fluorides in the discharge, contribute to the etching process[143].

Boron trifluoride (unlike the trichloride) is quite stable in electrical discharges. Nevertheless it can undergo changes under the influence of a discharge: thus, the yield of BF_2NH_2 by the reaction between BF_3 and ammonia can be increased markedly by activating the boron trifluoride in a microwave discharge of 80 W power[144].

Lower uranium fluorides are formed by the dissociation of uranium hexafluoride in a low-temperature plasma[145]. The stability of the discharge in UF_6 is determined by the gas pressure and by the frequency of the generator: at 10 MHz the discharge is stable up to 15–20 mmHg, at 17 MHz up to 30 mmHg, and at 2450 MHz frequency a stable discharge can be obtained at atmospheric pressure. The reaction of atomic fluorine generated in an h.f. discharge with uranium tetrafluoride has yielded up to 240 g h^{-1} of UF_6.[29] The fluorination of platinum with atomic fluorine gives PtF_6.[29]

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The reactions of fluorine and of the fluorides discussed above have been carried out in the non-equilibrium plasma of a glow discharge and of h.f., microwave and barrier discharges. The primary effect of an electrical discharge appears to be the generation of atomic fluorine by the dissociation of fluorine (or fluoride) molecules. The fluorine atoms then react with the other component, which may be located (in a gaseous or a condensed state) in the region where the fluorine atoms are generated or outside this region. Furthermore, the discharge may also activate the second component of the reaction (though this is not always a requirement in fluorination reactions). For example, the synthesis of O_2F_2 in an electrical discharge does not require special activation of the oxygen molecules, and the same is true of the fluorination of oxygen to O_2F_2 (in a reactor cooled in liquid nitrogen) by atomic fluorine generated on a nickel catalyst. Similarly, the synthesis of KrF_2 and XeF_2 in a glow discharge does not require activation of the krypton or xenon atoms.

The yield of the reaction products depends on several factors, such as the thermal stability of the product, its stability towards the discharge, and its inertness towards the apparatus walls. The thermally unstable compound O_2F_2, which has a vapour pressure of 0.01 mmHg at 105 K, condenses on the reactor wall when synthesised in a glow discharge and can be prepared in quantitative yield, whereas oxygen difluoride, though stable at up to ~480 K, has a vapour pressure of ~1 mmHg at 77 K and cannot be prepared in a glow discharge: it is not found among the products, possibly as a result of its decomposition in the gas phase under the influence of the discharge.

Fluorination in a discharge tends to give the higher fluorides, though the O + F system is exceptional in this respect and yields its highest and most stable fluoride (OF_2) only in a barrier discharge and in small yield. In the N + O + F and Cl + O + F systems only two members of the large group of oxide fluorides of nitrogen and chlorine have been obtained by plasmo-chemical methods: F_3NO and F_3ClO. This may be due to low stability of the other oxide fluorides in a glow discharge.

The equilibrium low-temperature plasma is not very attractive as a reaction medium for fluorine and the fluorides, though it could be used for pyrolysis reactions involving (for example) chlorofluorocarbon compounds.

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The Photochemistry of Bilirubin

A.E.Myshkin and V.N.Sakharov

The present state of research into the photochemical reactions of bilirubin in various media is examined. Data are presented on certain physical, chemical, and physicochemical properties of bilirubin. Attention is specially concentrated on photodynamic decomposition processes and photoisomerisation of bilirubin. The data are discussed in connection with the urgent problem of the use of light in the treatment of hyperbilirubinemia in children.
The bibliography includes 85 references.

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I. INTRODUCTION

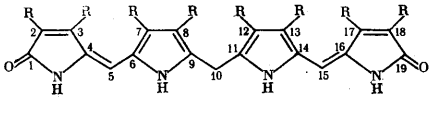
The yellow pigment bilirubin (BR) is formed in the organism mainly by the degradation of haemoglobin released into the blood plasma from decomposing erythrocytes. In contrast to the protein and "free" iron, which are also haemoglobin degradation products, BR is not utilised by the organism and furthermore can have a toxic effect on the latter. Therefore the removal of BR from the organism is an important physiological process, which, however, is to a large extent complicated by the insolubility of BR in aqueous media so that BR is transported in the organism by being bound in water-soluble complexes and as a result of the formation of water-soluble derivatives. In particular, BR circulates in the blood channels in a complex with serum albumin (SA) and with participation of liver cells is removed to the common bile ducts mainly in the form of esters with one or two glucuronic acid molecules. When the system for the removal of BR from the organism breaks down, a pathological state—hyperbilirubinemia—can arise; this state is accompanied by the deposition of BR in the skin, which acquires a yellow hue as a result. This factor is the basis for the common term "jaundice" used in medical practice.

Recently the treatment of neonatal jaundice by irradiating the skin with visible light in a specific wavelength range has come to be widely employed. The successful application of phototherapy led investigators to undertake studies on various aspects of the photochemistry of BR. This review is in fact devoted to this problem. Bearing in mind that in recent years there have been no review communications on BR in Soviet literature we also considered topics necessary for the understanding of the photochemistry of BR, which provide an idea about the most important physicochemical, physical, and chemical properties of BR.

II. THE STRUCTURE AND PROPERTIES OF BILIRUBIN

1. Structure

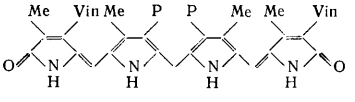
Bilirubin constitutes a set of structural isomers of a tetrapyrrole compound having the general formula



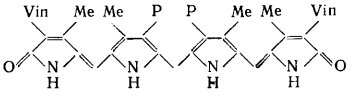
(1)

where R = methyl (Me), vinyl (Vin), or carboxyethyl (P = propionic acid residue) under conditions such that in all instances there are two vinyl, two carboxyethyl, and four methyl groups.

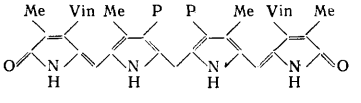
It has come to be assumed that only one of the structural isomers of BR (the so called BR IXα) is formed in the organism:



(IXα), (2)



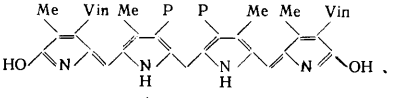
(IIIα), (3)



(XIIIα). (4)

This isomer has come to be referred to simply as bilirubin in medical, biological, and chemical practice. However, there are data showing that the blood serum of the newborn suffering from jaundice contains only 62–70% of BR IXα, while the remaining BR consists of the isomers IIIα (10–19%) and XIIIα (16–20%).[1]

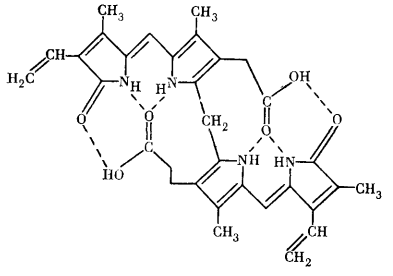
The bislactam or dioxo-form [formula (1)] is not the only possible form of BR. In principle one may assume also the existence of the bislactim form



(5)

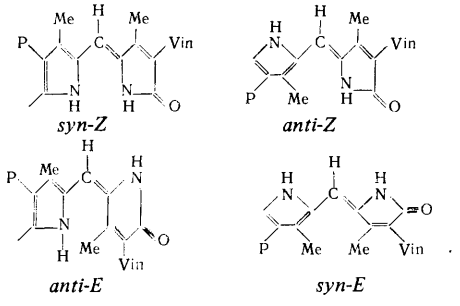
However, there are at present no reliable data concerning the content of a particular form both in solution and in the solid state. The bislactam form explains the majority of the chemical and physicochemical properties of BR but conflicts with the extremely low solubility of BR in water—at pH 7.4 and an ionic strength of 0.1 M the solubility of BR is only 0.05 mg litre^{-1}.[2] The contradiction disappears if one assumes the formation of a system of fairly strong intramolecular hydrogen bonds involving the propionic acid residues, the hydrogen atoms at the pyrrole nitrogen atoms, and the endocyclic carbonyl groups[3,4].

However, there are data showing that the hydrogen atoms at the pyrrole nitrogen atoms (and furthermore only in the two middle pyrrole rings) form hydrogen bonds only in non-polar solvents, while in the solid state of BR the four hydrogen atoms of the NH groups do not participate in the formation of intramolecular hydrogen bonds[5]. It has been suggested in addition that formula (6) corresponds to a planar conformation of the BR molecule[6], which has been confirmed by X-ray diffraction data[7]. Furthermore, the conformation of the BR molecule is chiral and its rigidity imparts to BR an optical activity[8]. The free energy barrier between the enantiomeric conformations of BR in chloroform, amounting to 17.9 ± 0.5 kcal mol^{-1}, has been determined by NMR.[9]



(6)

Together with structural and mirror isomerism, there is also a possibility of the *cis–trans* isomerism in the BR molecule, because the positions of the substituents relative to the two enamide C=C bonds can be different. The possible geometrical isomeric structures relative to only one of the C=C enamide bonds are illustrated below:



It has been shown by simple semiempirical conformational analysis[10] that the planar configuration holds only for the *syn-Z* isomer. Thus a structure of the type *syn-Z*, *syn-Z* should be ascribed to the planar conformation of the BR molecule. The isomerism associated with the rotation of the central pyrrole rings relative to the exocyclic C–C bond is usually neglected and the shorter designation *Z*, *Z* is used for the principal conformation of BR IXα.

2. Physicochemical Properties

Among the physicochemical properties of BR, its solubility in various media and the formation of complexes with other molecules are of greatest interest for photochemical investigations. Furthermore, the knowledge of these characteristics of BR is significant for the understanding of its behaviour in the organism at various metabolic stages.

The extremely low solubility of BR in water has already been mentioned. Since BR has two amide carbonyl groups and, what is still more significant, two carboxy-groups, the pH of the medium is of decisive importance for the solubility of BR in aqueous media. With increase of pH, the carboxy-groups ionise initially and then the enolic groups, which facilitates the solubilisation of BR in water. It is believed that 0.1 M NaOH, KOH, or Na_2CO_3 are optimal for the preparation of aqueous BR solutions. Potassium cyanide also promotes the dissolution of BR: 0.04 M BR dissolves in 0.1 M KCN.[6] When aqueous BR solutions are neutralised, colloidal solutions are formed. In acid solutions BR is almost insoluble. The majority of non-polar organic solvents do not dissolve BR. Polar solvents such as methanol, ethanol, and acetic acid are also included among solvents which are ineffective for BR. On the other hand, BR readily dissolves in acetone, benzene, isobutyl methyl ketone, formamide, dimethylformamide (DMF), dimethyl sulphoxide (DMSO), pyridine, and chloroform[6]. Chloroform has come to be particularly widely used by investigators.

A recently published communication[11] presents data contradicting the widespread concept of the lipophilicity of BR and its consequent neurotoxicity. The author[11] showed that the solubility of BR in triglycerides is low and that its solubility increases with increasing polarity of the medium.

The solubility of BR in aqueous solutions of proteins, particularly blood serum albumins, is of particular importance. It is noteworthy that proteins themselves are incapable of solubilising BR in aqueous solution. When it is necessary to dissolve BR in a neutral aqueous solution of a protein, BR is usually first dissolved in an alkine solution of the protein, which is then neutralised. It follows from this that proteins are incapable of disrupting the intramolecular hydrogen bonds in the BR molecule. On the other hand, proteins form fairly stable complexes with BR in which the above bonds had been ruptured beforehand[6].

Numerous studies have been made on the formation of complexes between BR and SA. It has been established that serum albumins possess centres for "strong" and "weak" binding of BR.[12,13] Between one and two BR molecules are strongly bound to SA and between 10 and 14 molecules are less strongly bound[13]. The less strongly bound BR molecules are comparatively readily displaced from the complexes by carboxylic acids[14–16] and also by certain other compounds.

3. Chemical Properties

In considering the structure of the BR molecule, a number of *a priori* conclusions can be reached concerning the most general possibilities for its chemical reactions. In the first place the BR molecule can be regarded as consisting of two conjugated fragments separated by a methylene bridge. Hence it is natural to suppose that the latter is a fairly active reaction centre, since, as a result of the possible dehydrogenation of BR at the bond adjoining this bridge, the conjugation embraces the entire tetrapyrrole system, which should lead to a gain in its energy. The presence of a large number of double bonds, including four exocyclic carbon–carbon double bonds, leads to the expectation of various addition reactions of BR involving the double bonds and also of oxidative cleavage reactions typical for olefins. The propionic acid residues are responsible for the weak acid properties of BR, which can be intensified in an alkaline medium as a result of the tautomeric transition of BR to the bislactim form with two enolic hydroxyls. The basic properties of BR are determined by the nitrogen atoms

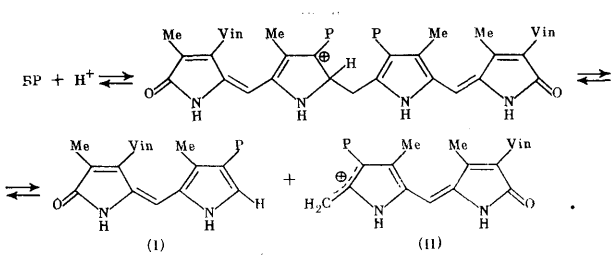
in the central pyrrole rings. In the extreme pyrrole rings the nitrogen atoms, which are of the amide type, are not basic.

Strong oxidants, such as potassium permanganate or chromic acid in acetic acid[17], decompose the tetrapyrrole system to monopyrrole compounds, from a mixture of which haematinic acid and methylvinylmaleimide were isolated. Weaker oxidants, such as iodine, a dilute solution of iron(III) chloride[18], cerium salts, or hydroquinone in an alkaline medium[19] oxidise only the central methylene bridge of BR with formation of a biliverdin molecule [see compound (V) below].

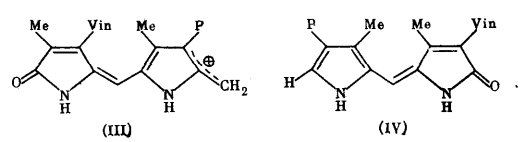
The reduction of BR is possible only with the aid of strong reductants. In the catalytic hydrogenation of BR in the presence of colloidal palladium or platinum in an alkaline medium[20], the vinyl group in the 18-position and then the vinyl group in the 3-position were reduced in succession (the formation of mesobilirubin), after which the $C_{(5)}$ and $C_{(15)}$ methylidene bridges were reduced under more severe conditions (the formation of urobilinogens). Sodium amalgam has also been used to reduce BR.[21,22].

The behaviour of BR in the presence of acids is interesting from all points of view. It has been observed[23] that, as a result of the acidification of a solution of BR IXα in DMSO with dry hydrogen chloride at room temperature, a mixture of BR isomers is formed after 1 min: IXα, IIIα, and XIIIα in proportions of 1:2:1. The isomerisation in the DMSO–acetic acid system takes place only on heating. In an alkaline medium (DMSO–NaOH–water) isomerisation was not observed.

On the basis of the products of the acid isomerisation of BR IXα, it is easy to postulate a process mechanism which apparently involves the protonation of the BR molecule at the $C_{(9)}$ or $C_{(11)}$ atoms with subsequent cleavage of the protonated BR molecule into two dipyrrolylmethene fragments. In particular, protonation at $C_{(9)}$ leads to the following transformations of BR IXα:



The protonation at $C_{(11)}$ similarly results in the formation of two fragments:



The recombination of (I) and (II) (the reverse reaction) leads to the reformation of the isomer BR IXα. On the other hand, the recombination of (I) and (III) and of (II) and (IV) leads to the BR isomers IIIα and XIIIα respectively.

A physiologically important reaction of BR is the formation of its water-soluble esters via the propionic acid residues, in particular the formation of esters with glucuronic acid. The mono- and di-glucuronides of BR have been obtained from BR with imidazole-activated carboxy-groups[24].

Numerous studies have been devoted to the formation of metal complexes of BR,[25–27] but these properties of BR are considerably outside the subject of the present review.

4. Optical Absorption Spectra

The optical characteristics, particularly the absorption spectra, of BR are important for the understanding of the mechanism of its photochemical reactions. According to data in a review[6], the absorption spectrum of a neutral aqueous solution of BR has a maximum at 440 nm, the transition to the alkaline region being accompanied by a significant hypsochromic shift (λ_{max} = 420 nm). When proteins are added to an alkaline solution of BR, the absorption maximum shifts towards longer wavelengths (450 nm), approaching the position of the maximum in a neutral protein-free solution. This factor suggests a definite similarity between the states of BR in a protein-free aqueous solution and in the presence of proteins. Since, as stated above, the formation of complexes between BR and proteins requires a preliminary dissociation of the intramolecular hydrogen bonds in the BR molecule, presumably the BR in complexes with proteins has no or virtually no bonds of this kind. On the other hand, the similarity of the spectra permits an analogous conclusion also concerning BR in a protein-free aqueous solution. The same state is apparently characteristic also of BR dissolved in chloroform (λ_{max} = 453 nm) and DMF (λ_{max} = 456 nm). The available data concerning the absorption of BR in the ultraviolet are contradictory owing to the different degrees of purity of the pigment investigated. One of the causes of this is the relatively low stability of BR in solutions. For example, the optical density at the BR absorption maximum in 0.1 M NaOH, NH_4OH, and Na_2CO_3 solutions decreases at a rate of 2–10% per hour[28]. It is therefore recommended that the ultraviolet and visible spectra of BR be measured in the course of several minutes after preparing the solution.

The infrared spectrum of BR in KBr contains the absorption band of the hydroxyl in the carboxy-group at 2500 cm^{-1} and of the carbonyl group at 1680 cm^{-1}. The bathochromic shift of the carbonyl band is due to the involvement of the carbonyl group in a hydrogen bond[29].

5. The Luminescent Properties

The luminescent properties of BR provide the best idea about the nature of the excited states of the molecule, which in its turn permits a deeper understanding of the photochemistry of BR and the associated problems of phototherapy. Neither the fluorescent nor the phosphorescence of BR solutions has been observed at room temperature. On the other hand, a greenish emission at ~525 nm has been noted in various polar solvents at 77 K.[30] The fluorescence quantum yield Q_F = 0.13 has been determined in ethanol at 77 K.[31]

The fluorescence of BR in the ether–isopentane–ethanol–DMF (6:5:3:0.5) system with excitation by the light of a high-frequency pulsing lamp at a wavelength <450 nm has been studied in detail[32]. The emission half-period was <5 ns, which is characteristic of fluorescence. The apparent fluorescence quantum yield (relative to fluorescein at room temperature) was ~0.05. The excitation spectrum, measured at the emission maximum at 520 nm, revealed a fairly sharp maximum at 472 ± 5 nm, which differed significantly from the broad band in the region of 470 nm in the absorption spectrum at room temperature. In their study of the influence of temperature in the range from 293

to 215 K on the absorption of BR in dichloroethane and DMF at 450 nm, the authors[32] observed spectral changes only for the solution in DMF. At the same time a fluorescence appeared in the DMF solution at 215 K, such fluorescence being absent from dichloroethane at the same temperature. On this basis, it was suggested[32] that a fluorescent form of BR is formed reversibly in certain polar solvents, particularly DMF, as the temperature is reduced.

Later it was observed that the fluorescence of a BR solution is possible also at room temperature when the solution contains SA with which BR forms a complex. Depending on the origin of the SA, both the emission maximum and the fluorescence quantum yield can vary[33]. Whereas in the case of human SA these parameters are respectively 527 nm and 0.00102, for bovine, rabbit, and monkey SA their respective values are 546 nm and 0.00085, 531 nm and 0.00084, and 528 nm and 0.00037. However, a higher fluorescence quantum yield of the complex of BR with bovine SA has been published[31] ($Q_F = 0.01$).

Thus a solution of BR, which does not fluoresce at room temperature, begins to fluoresce only when the temperature is reduced on formation of a complex of BR with a protein. In both cases light is emitted by a BR molecule, which has a limited number of degrees of freedom. Matheson et al.[31] therefore reached the fully logical conclusion that the radiationless loss of energy by BR in a liquid solution is determined by molecular vibrations or conformational changes, which completely suppress the emission. This conclusion has been to some extent confirmed by the observation of the fluorescence of BR in an aqueous solution in the micellar environment of cetyltrimethylammonium bromide molecules[34].

The absence of the fluorescence of BR under the usual conditions has been explained[35] by the rapid internal transition ($k \cong 10^{12}$ s^{-1}) of the excited singlet state S_1 formed initially into a state S_1' with a somewhat lower energy, which can undergo a radiationless transition either to the initial singlet state S_0 or to the first excited triplet state T_1, which will be considered later.

III. PHOTOCHEMICAL REACTIONS OF BILIRUBIN

1. Primary Photochemical Reactions

The photoexcited BR undergoes reactions giving rise to products which can in their turn undergo further reactions both under the influence of light and in the dark. In order to approach an understanding of the mechanisms of the photochemical reactions of BR, it is useful to consider separately the primary photochemical reactions and to attempt to isolate them from the overall chain of transformations of BR in the light. We shall introduce a more rigorous limitation by assuming that other molecules, including molecular oxygen, are not involved in the primary photochemical reactions of BR.

By irradiating with light from monochromatic and nonmonochromatic xenon sources a solution of BR in chloroform and also in phosphate buffer at pH 7.4, placed in a quartz cuvette, Davies and Keohan[36] observed by differential spectroscopy the presence of a photolabile product with an absorption maximum at 490 nm. The product could be detected only in the presence of an excess of BR, which played the role of a protecting material (internal filter). This experiment was subsequently reproduced by the same authors[37] using apparatus which permitted the isolation of the exciting emission with a maximum in the range 410–440 nm, having a low energy both below 360 nm and above 470 nm; in particular, this created conditions for a greater stability of the photoproduct with an absorption maximum at 490 nm. It was observed that the photoproduct concentration increases up to a BR conversion of 10–15% and then remains constant.

After a careful analysis of the differential spectra, the authors[37] concluded that, together with the photoproduct having $\lambda_{max} = 490$ nm, a second photoproduct, absorbing at 420 nm, is formed. The similarity of the differential spectra of seemingly different systems such as BR solutions in carbon tetrachloride and chloroform, on the one hand, and a solution of BR in phosphate buffer with added bovine SA, on the other, is noteworthy. In contrast to this, the differential spectrum of an irradiated BR solution in phosphate buffer with added human SA has its own characteristic features. Hence one may conclude that, in contrast to bovine SA, human SA modifies significantly human BR.

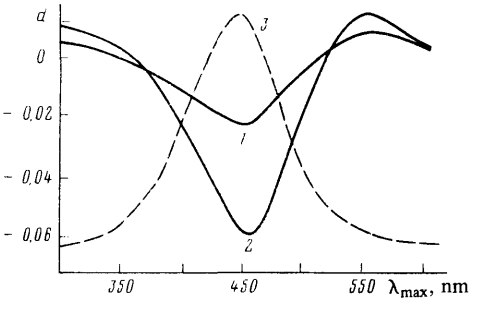


Figure 1. Differential spectra of a solution of BR in chloroform with 1% of ethanol on irradiation at a wavelength of ~440 nm: *1*) 60 s after irradiation; *2*) 360 s after irradiation; *3*) integral spectrum of BR (on an arbitrary scale).

On irradiating BR in chloroform with added 1% of ethanol at a wavelength of ~440 nm, Lightner et al.[38] observed a positive absorption in the region of 350 and 500 nm in the differential spectra (Fig.1) together with a negative maximum at ~460 nm (corresponding to a decrease of the amount of BR). Analogous spectra have also been obtained after irradiating BR solutions in chloroform with 1% of hexane at 420 and 430 nm and also in ammoniacal methanol at 400, 410, and 420 nm. It is significant that the absorption band at ~500 nm arises under both anaerobic and aerobic conditions. The absence of an effect by singlet oxygen in the latter case has been demonstrated by the weak influence on the spectrum by singlet oxygen fluorescence quenching agents—dimethylbutene, diethylamine, and triethylamine. The intensity of the band at ~500 nm gradually increases in the course of irradiation and reaches a constant value after 1–10 min (alkaline solvents accelerate the process). Under more prolonged irradiation, the intensity of this band begins to diminish. If a solution which has reached photoequilibrium is allowed to stand in the dark at 22 °C, a slow but quite appreciable thermal restoration of the initial spectrum takes place. This process is accelerated by the addition of traces of CF_3COOH (the reduction then takes place almost instantaneously) or I_2. An analogous effect also occurs on irradiation of a photoequilibrated solution by light at a

wavelength of ~510 nm with a band width of 10 nm. In the latter case a new photostationary state of the solution with a lower content of the photoproduct arises.

The authors[38] were able to isolate with the aid of thin-layer chromatography the photoproduct formed on irradiation of the BR solution in ammoniacal methanol. The product, which the authors called photobilirubin, consisted of a yellow substance with a broad absorption band at 440 nm but without an absorption peak in the region of 500 nm. Photobilirubin was always contaminated with different amounts of BR, which the authors believe is formed via a reverse thermal transformation of photobilirubin into BR. According to Lightner et al.[38], the peak at 350 and 500 nm in the differential spectra are not absorption maxima of the photoproduct and merely characterise the difference between the absorption of BR and that of the photoproduct in the region of the above wavelengths. The logical hypothesis was put forward that photobilirubin is none other than a mixture of the photoisomerisation products of BR involving the exocyclic C=C enamide bonds, among which the virtually identical *Z*, *E*-, and *E*, *Z*-isomers predominate and there is a small amount of the *E*, *E*-isomer (see the formulae above).

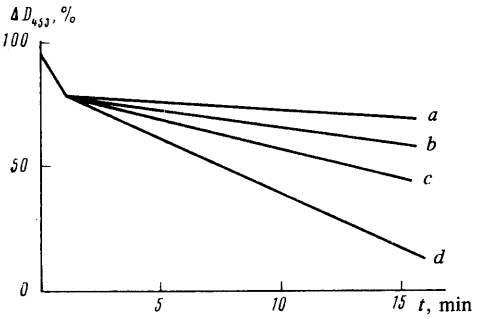


Figure 2. Decrease of the concentration of BR on irradiation of its solution in chloroform (at a concentration of 1.5×10^{-2} M) from a light source at a wavelength >390 nm (for explanation, see text).

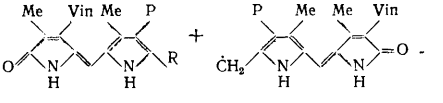
Fig. 2 presents curves characterising the decrease of the BR concentration (decrease of absorption at 453 nm) observed in chloroform solution by light at a wavelength >390 nm.[38] Solutions saturated with argon (*a*), saturated with O_2 in the presence of 0.15 M 1,4-diazabicyclo[2,2,2]octane (*b*), saturated with O_2 in the presence of 10^{-3} M dimethylbutene (*c*), and simply saturated with O_2 (*d*). Evidently all the curves have a common initial section, to which corresponds an irradiation time of ~1 min. The authors[38] suggest that this section characterises the formation of photobilirubin, while the subsequent sections of the individual curves characterise the conversion of BR, the rate of which depends on the mixture composition.

Products similar to the photobilirubin found by Lightner et al.[38] have been discovered also by other workers. In particular, Zenone[39] et al., who irradiated BR in chloroform with visible light, isolated in 7% yield a yellow product with a higher polarity than BR IXα. After irradiating with intense visible light a solution of BR in chloroform, Stoll et al.[40] isolated three BR isomers having the same absorption maximum (442 nm) as BR IXα (the *Z*, *Z*-isomer). Two of these isomers decomposed in the dark with formation of brown products, while the third was reconverted into the initial BR. On irradiation, all three isomers were converted into the *Z*, *Z*-isomer BR IXα.

The studies discussed above permit a conclusion very important for the understanding of the photochemistry of BR: the primary products arising on irradiation of BR with visible light are its geometrical isomers. Possibly one of the causes of the absence of the BR fluorescence and phosphorescence under the usual conditions is the consumption of the excess energy of the excited singlet and triplet states on overcoming the energy barrier separating the *Z*, *Z*-isomer of BR from the other geometrical isomers. Being less stable than the *Z*, *Z*-isomer, these isomers are either reconverted into the initial BR or are irreversibly converted into non-BR products, depending on the conditions. A particularly important property of the BR "photoisomers" is their polarity, which is apparently determined by the complete or partial rupture of the intramolecular hydrogen bonds characteristic of the *Z*, *Z*-isomer of BR. The polarity is responsible for the water solubility of these isomers, which may prove to be one of the decisive factors in the phototherapy of the jaundice of the new-born.

2. Photochemical Formation of Structural Isomers of Bilirubin

As already stated, in the presence of an acid BR IXα isomerises to its structural isomers IIIα and XIIIα. The first stage of the process is the protonation of the BR molecule at the $C_{(9)}$ or $C_{(11)}$ atoms. On the basis of general chemical considerations, one may assume that an analogous reaction can proceed also via a radical mechanism. If a free radical $\dot{R}$ arises for one reason or another in a solution containing BR IXα, one of the possible reactions will be its addition to the BR molecule at $C_{(9)}$ or $C_{(11)}$. Each of the newly formed tetrapyrrole free radicals can decompose into two dipyrrole fragments, for example [after addition to $C_{(9)}$]:



The radical fragment can in its turn add to an unreacted molecule of BR IXα at $C_{(9)}$ or $C_{(11)}$ (chain propagation), after which the dipyrrole fragment, incorporated in the initial molecule, can be split off in the form of a free radical from the hexapyrrole free radical formed, etc. As a result, a further two isomers (IIIα and XIIIα) will be produced instead of the isomer BR IXα present initially in this system. The primary radical $\dot{R}$ can be formed from any one component of the system, including a BR molecule. One of the factors stimulating the generation of free radicals is irradiation by light.

Photoisomerisation of the type IXα ⇌ IIIα ⇌ XIIIα has indeed been frequently observed experimentally. In particular, McDonagh[41] observed this isomerisation after irradiating with visible light solutions of BR IXα (2.5 mg %) in aqueous buffers at pH 8.0 and 8.5 in the absence of O_2. The reaction proved to be less typical for a solution of BR in chloroform and did not occur at all in 0.1 *N* aqueous NaOH solution in DMSO.

The photoisomerisation of BR IXα to its structural isomers is probably one of the causes of the usual contamination of commercial BR preparations by isomers IIIα and XIIIα.

3. Interaction of Bilirubin with Molecular Oxygen on Photoirradiation

Since the photochemical reactions of BR under physiological conditions always take place in the presence of molecular oxygen, studies of the photochemistry of BR in oxygen-containing solutions and, specifically the interaction of BR with O_2 under photoirradiation conditions, are of greatest interest from the practical point of view.

McDonagh[42] was the first to show that BR sensitises the formation of singlet oxygen. He established that, when BR is irradiated with visible light in chloroform, its photochemical oxidation is greatly accelerated by Methylene Blue, octaethylporphin, and other agents photosensitising the formation of $^1O_2$, while $^1O_2$ quenching agents—1,4-diazabicyclo[2,2,2]octane and *trans*-β-carotene—inhibit photochemical oxidation. McDonagh[42] suggested that the photochemical oxidation of BR by molecular oxygen proceeds via a stage involving energy transfer from the excited triplet BR to $^3O_2$. Another piece of evidence for the participation of singlet oxygen in the reaction (predominantly in the $^1\Delta g$ state) is the similarity of the rate constant for the reaction of BR with photophysically generated $^1O_2$ in water (3.5×10^8 litre mol^{-1} s^{-1}) to the rate constants for the photochemical oxidation of BR in chloroform, a mixture of chloroform and methanol, and other solvents. The rate constant for the physical quenching of the fluorescence of bilirubin by $^1O_2$ has been determined as 9×10^8 litre mol^{-1} s^{-1}.[37]

The existence of the triplet state of BR has been demonstrated experimentally[43]. A solution of BR at a concentration of 4×10^{-5} M in benzene with added 0.1 M biphenyl was subjected to pulse radiolysis with a dose of ~1000 rad, after which the absorption spectrum of the excited BR was measured. It was observed that, over the entire range of the experimental spectrum (490–700 nm), after a 20 ns excitation pulse the absorption intensity uniformly increases to a maximum after 5 μs, and then decreases with a half-life of 9 μs. The rate of increase of absorption is the same as the rate of decomposition of the triplet state of biphenyl measured at 360 nm.

An analogous but weaker absorption arises also in the pulse radiolysis of BR in the absence of biphenyl. After adding 10^{-5} M BR to a solution of anthracene in benzene (at a concentration of 3×10^{-5} M), the author[43] noted an appreciable increase of the rate of decomposition of the triplet state of anthracene, whence it follows that the triplet level of BR is lower than that of anthracene. It has also been established that the triplet level of BR is close to that of perylene and has an energy of ~150 kJ mol^{-1}. The yield of the singlet–triplet transition $\phi_T \leq 0.1$ has been determined by laser flash photolysis using anthracene as a standard. The proposed mechanism of the photochemical oxidation of BR includes the following stages:

$$\mathrm{BR} \rightarrow {}^1\mathrm{BR}^*,$$

$${}^1\mathrm{BR}^* \rightarrow {}^3\mathrm{BR}^*,$$

$${}^3\mathrm{BR} + \mathrm{O}_2({}^3\Sigma_g^-) \rightarrow \mathrm{BR} + \mathrm{O}_2({}^1\Delta_g),$$

$$\mathrm{O}_2({}^1\Delta_g) + \mathrm{BR} \rightarrow \text{BR oxidation products}.$$

Since the energy of the $O_2(^1\Delta_g)$ molecule is 94 kJ mol^{-1} and the energy of ^{3}BR* is ~150 kJ mol^{-1}, the reverse energy transfer from $O_2(^1\Delta_g)$ to BR in the ground state with excitation of BR in the triplet state is impossible. The quenching of singlet oxygen in its interaction with BR is therefore accompanied by chemical transformations of BR. On the other hand, agents quenching singlet oxygen, having an energy between 150 and 94 kJ mol^{-1}, can inhibit the decomposition of BR, as suggested by Land[43]; the inhibition takes place via energy transfer from the triplet state of BR. Quenching agents with energies less than 94 kJ mol^{-1} can inhibit the decomposition of BR both as a result of energy transfer from its triplet state and as a result of the quenching of the singlet oxygen (depending on the relative concentrations of O_2 and the quenching agent). As regards sensitisers, those whose energy exceeds 150 kJ mol^{-1} can facilitate the formation of ^{3}BR* mainly before the sensitisation of the formation of $O_2(^1\Delta_g)$. On the other hand, sensitisers with energies between 150 and 94 kJ mol^{-1} can only excite the formation of $O_2(^1\Delta_g)$.

Matheson et al.[35] investigated the influence of various factors on the quantum yields (ϕ) of the photochemical oxidation of BR using its dilute solutions—$(0.5–5) \times 10^{-3}$ M. The latter factor prevented the formation of biliverdin, which is favoured by high BR concentrations. It was established that ϕ increases with increasing O_2 concentration in chloroform, methanol, Freon-113, and water. In aqueous solution ϕ increases with increase of pH from 7 to 11. The following mechanism of the photochemical transformations of a general singlet oxygen acceptor (A) has been proposed:

$$\mathrm{A} \rightarrow {}^1\mathrm{A}\ ,$$

$${}^1\mathrm{A} \xrightarrow{k_1} \mathrm{A}\ ,$$

$${}^1\mathrm{A} \xrightarrow{k_2} {}^3\mathrm{A}\ ,$$

$${}^1\mathrm{A} + {}^3\mathrm{O}_2 \xrightarrow{k_3} {}^3\mathrm{A} + {}^3\mathrm{O}_2\ ,$$

$${}^1\mathrm{A} + {}^3\mathrm{O}_2 \xrightarrow{k_4} {}^3\mathrm{A} + {}^1\mathrm{O}_2\ ,$$

$${}^3\mathrm{A} + {}^3\mathrm{O}_2 \xrightarrow{k_5} \mathrm{A} + {}^1\mathrm{O}_2\ ,$$

$${}^3\mathrm{A} \xrightarrow{k_6} \mathrm{A}\ .$$

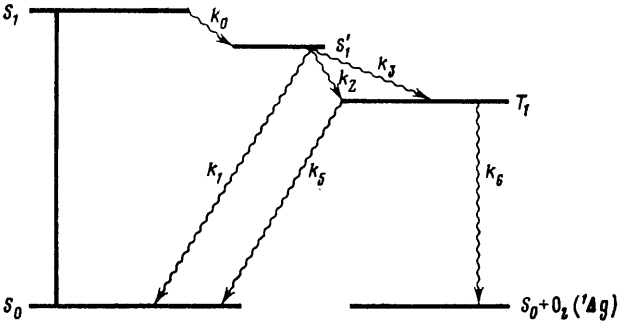


Figure 3. The energy levels of BR on photoexcitation in the presence of O_2; transitions with the rate constants k_3 and k_4 take place in the presence of $^3O_2$.

In the case of BR the rate constant k_4 can be neglected, since the energy of the singlet–triplet cleavage for BR (the difference between the energy of ^{1}BR*, which is 240 kJ mol^{-1},[31] and the energy of ^{3}BR*, which is ~150 kJ mol^{-1} [43]) is ~90 kJ mol^{-1}, which is less than the energy of $O_2(^1\Delta_g)$ (94 kJ mol^{-1}). The constant k_3 is largely determined by diffusion and should therefore be much less than

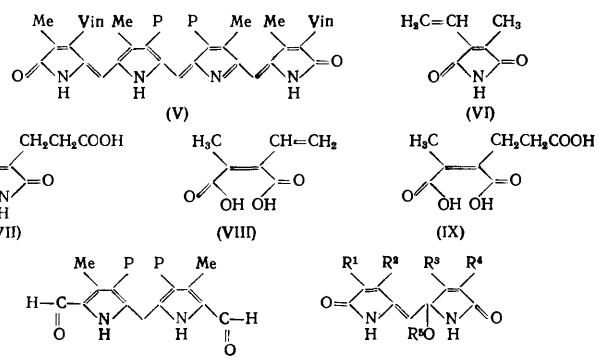
k_1. However, this is true only in chloroform solution, while in other solvents $k_3 > k_1$. On this basis, the authors[35] concluded that the state relaxing with the rate constant k_1 is not the excited singlet state formed initially. A scheme of the interlevel transitions in the photoexcitation of BR and in the relaxation of the excited BR state in the presence of O_2, illustrated in Fig.3, has been proposed. According to this scheme, the state S_1 formed initially is very rapidly converted into the non-fluorescent state S_1'.

The quantum yields of the excitation of BR to the triplet state in various media have been measured in a recently published study[44] (using laser flash photolysis at a wavelength of 347 nm). In particular, in an aqueous solution at pH 9–11 and in ammoniacal methanol the quantum yield was less than 0.005. In a non-polar medium (benzene) $\phi \cong 0.001$. The addition of triethylamine to benzene lowered ϕ to less than 0.005.

4. Photochemical Oxidation of Bilirubin

Many workers have frequently noted that the photodegradation of BR in the presence of atmospheric oxygen proceeds much more rapidly than in its absence. As already stated in a previous section, the first stage of the photochemical oxidation of BR is the photoexcitation of its molecule to the triplet state (arising as a result of the intercombination transition from the excited singlet state of BR). The half-life of the state (9 μs) is entirely sufficient for the transfer of the triplet energy to the molecular oxygen. The singlet oxygen formed under these conditions can react in its turn with a BR molecule in the ground state, oxidising it. Thus BR is, on the one hand, a photosensitiser of the formation of molecular oxygen and, on the other hand, it is an acceptor of singlet oxygen. The photochemical oxidation of BR by molecular oxygen has therefore come to be regarded as self-sensitised.

The composition of the products of the photochemical oxidation of BR depends greatly on the medium in which the process takes place. In protic solvents (usually in ammoniacal methanol, ethanol, and water) different workers have detected biliverdin (biliverdin IX) (V), methylvinylmaleimide (VI), haematinimide (VII), methylvinylmaleic acid(VIII), haematinic acid (IX), dipyrroledialdehyde (X), and the adducts of propentdyopents (XI), whose formulae are given below:

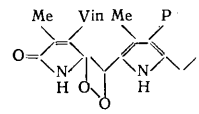


(V) (VI) (VII) (VIII) (IX) (X) (XI)

(XI): (a) R^1, R^3=Me; R^3=Vin; R^4=P; (b) R^2, R^3=Me; R^1=Vin; R^4=P; (c) R^2, R^3=Me; R^4=Vin; R^1=P; (d) R^2; R^4=Me; R^3=Vin; R^1=P; R^5=H, Me or Et.

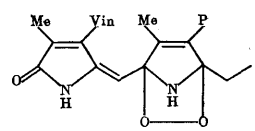
The green pigment biliverdin is the product of the oxidation of the methylene bridge in the BR molecule, which can be achieved fairly readily and occurs even in the dark, albeit at a low rate[45]. The formation of biliverdin from BR also in the absence of oxygen is known[46]. The ease of the conversion of BR into biliverdin served as a basis for the hypothesis that biliverdin is an intermediate in the more far-reaching photodegradation of BR.[47,48] However, there is serious evidence against this claim. After irradiating the dimethyl ester of biliverdin in chloroform (biliverdin itself is sparingly soluble in chloroform), McDonagh[49] established that the biliverdin ester does not sensitise the excitation of oxygen. Comparative experiments with irradiation by visible light showed that the photodegradation of BR is significantly faster than that of the dimethyl ester of biliverdin[49,50]. On the other hand, it has been established that the dimethyl ester of biliverdin is in the first place, like BR, a quenching agent for singlet oxygen and, in the second place, a much poorer $^1O_2$ acceptor than BR.[49] Being a $^1O_2$ quenching agent while at the same time undergoing very slow oxidation, biliverdin therefore inhibits the photochemical oxidation of BR, while the main BR oxidation pathway does not involve the intermediate formation of biliverdin.

Methylvinylmaleimide is formed[47,51] as a result of the attack by singlet oxygen on the exocyclic C = C bond in the 4- or 15-position in the BR molecule with the intermediate formation of a four-membered peroxide ring:



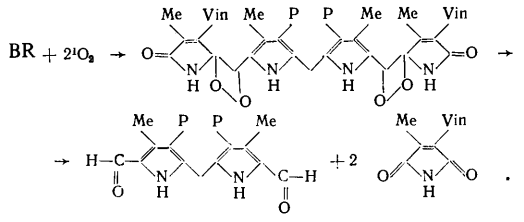
While the detection of methylvinylmaleimide *in vitro* in alcoholic solutions suggested that it can be formed also in the organism, this hypothesis became more definite after its detection also in a number of BR photochemical decomposition products in an aqueous buffer[52]. Under the influence of light, methylvinylmaleimide undergoes further degradation and the process takes place even in the absence of oxygen, albeit more slowly. The methylvinylmaleimide degradation products have not been determined, but it has been suggested that they can be oxidised to methylcarboxymaleimide, the decarboxylation of which can lead in its turn to the formation of methylmaleimide[53]. The latter is a modifying agent for proteins and can interfere with their normal functioning in the organism.

The formation of the imide of haematinic acid is apparently preceded by the interaction of O_2 (dienophile) with the conjugated diene system of one of the central pyrrole rings in the BR molecule, which results in the formation of a peroxide adduct having the following structure[54]:

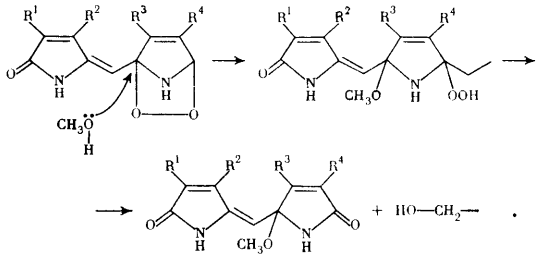


The appearance of methylvinylmaleic and haematinic acids in solutions is a natural consequence of the hydrolysis of the corresponding imides either in the photochemical reaction or in the treatment of the reaction mixture. The dipyrroledialdehyde detected in the reaction mixture[50,54] can be formed by a reaction of the same type as that leading to the formation of methylvinylmaleimide: the interaction of molecular oxygen with the double bonds in the 4- and 15-positions of BR. Theoretically the formation of a single dipyrroledialdehyde molecule is accompanied by the formation of two molecules of

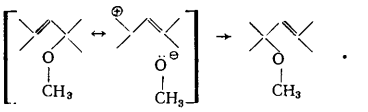
methylvinylmaleimide[55]:



A considerable proportion of the BR photochemical oxidation products in protic solvents consist of adducts of propentdyopents with the corresponding solvent. The mechanism proposed[56] for the formation of adducts of propentdyopents in an ammoniacal methanol solution includes the preliminary formation of an endoperoxide—the product of the diene condensation of O_2 with the diene system of the second or third pyrrole ring—and subsequent methanolysis of the endoperoxide and the decomposition of the intermediate hydroperoxide:



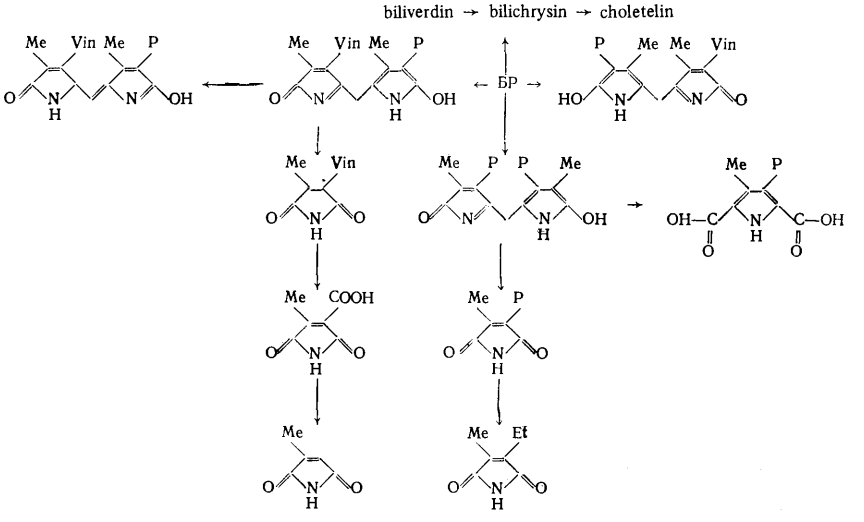
Bearing in mind that the irradiation of BR IXα with light results in the formation of its equilibrium mixture with the isomers IIIα and XIIIα, it follows that, in conformity with the above scheme, each BR isomer should form on irradiation in methanol the corresponding methanol adducts of propentdyopents: IXα–propentdyopents (a and b), IIIα–propentdyopent (b), and XIIIα–propentdyopent (a). However, the formation of propentdyopent (a) was not confirmed in a later study[51]. Together with product (b), its isomers (c) and (d), which are not formed directly from BR IXα and its two isomers via the scheme proposed by Bonnett[56], were detected in the reaction mixture. In model experiments the propentdyopents (b) and (c) were obtained from the pure isomer BR IIIα, while propentdyopent (d) was obtained from BR XIIIα. Thus the formation of a mixture of propentdyopents (b), (c), and (d) from the irradiated BR IXα can be explained, on the one hand, by the photoisomerisation of BR IXα to IIIα to XIIIα and, on the other hand, by the isomerisation of the methanol adducts of the propentdyopents already formed, consisting in the transfer of the methoxy-group via one carbon atom to a neighbouring pyrrole ring with the simultaneous migration of the double bond (the allyl rearrangement):



The isomerisation of the propentdyopent adducts isolated has been confirmed experimentally[51]. On the other hand, the absence of propentdyopent (a) from the reaction mixture is apparently due to the marked shift of the equilibrium (a) ⇌ (d) to the right.

Numerous studies have been made on the photochemical oxidation of BR using its solutions in chloroform[28,42,53,57]. The appearance, together with biliverdin, of vicinal diols, formally representing the products of the hydroxylation of biliverdin at the non-vinyl exocyclic C=C bonds, has been noted in this solvent[57,58]. It has been suggested that the above compounds are produced as a result of the interaction of the excited BR with triplet oxygen. A smaller yield of the di- and mono-pyrrole oxidation products, compared with that observed in reactions in protic solvents was also noted[59,60]. Fundamental differences between the nature of the photochemical oxidation of BR in solutions in chloroform and carbon tetrachloride were not observed despite the difference between the polarities of these solvents. The differential spectra characterising the changes in these solutions on irradiation with light having a band maximum at 410–440 nm were in broad outline the same[37].

In a study of the photochemical oxidation of BR in chloroform under the influence of scattered sunlight over a long period (500 days), Gray et al.[53] isolated various products at different stages of the process, which enabled them to set up a scheme of the probable transformations of BR (see below).



The authors[53] established with the aid of paper chromatography that BR disappears completely from the reaction mixture after 12–25 days (depending on the intensity of illumination). Biliverdin, whose concentration in the mixture never exceeded 13% of the initial BR concentration, disappeared after 40–50 days. On the hundredth day the solution became almost colourless. The observed stability of BR in chloroform under a nitrogen atmosphere led to the conclusion that most of the BR decomposes via oxidation with molecular oxygen.

Gray et al.[53] also compared the BR photodegradation pathways in various solvents. In particular, they noted that in a methanol–chloroform mixture, weakly alkaline methanol and aqueous solutions, BR decomposes with rapid breakdown of the tetrapyrrole structure, as in chloroform solutions. On the other hand, in acid media the decomposition of the tetrapyrrole structure proceeds with much difficulty: propentdyopents, imides, and dipyrrolylmethenes were detected only in weakly acid solutions. Furthermore, the overall rate of decomposition of the BR in acid solutions is lower than in alkaline solutions.

A number of studies have been devoted to the photochemical oxidation of BR in the presence of serum albumin[36,48,61]. On the one hand, a complex of BR with SA is formed in a living organism and is of special interest. On the other hand, this complex is soluble in water, which makes it possible to investigate the behaviour of BR on photoirradiation in neutral aqueous solutions. By varying the pH of the medium in the range 7.4–13.0, Ostrow and Branham[48] established that in a neutral medium SA accelerates the photochemical decomposition of BR, while in an alkaline medium it retards it. It has also been noted[61] that BR becomes more polar in the course of irradiation and that its bond with the protein is consequently weakened. The photochemical oxidation of SA was not observed at the given stage. However, by irradiating the complexes of BR with human and bovine SA in aqueous solution at pH 7.4, Rubatelli and Jori[62] observed changes, occurring as a result of the photodynamic effect, apparently in the two histidine residues in both albumins. The authors suggest that these changes do not alter the tertiary structure of the proteins but decrease their binding capacity in relation to BR. It was also noted that the tertiary structure of bovine SA is more labile than that of human SA.

As already mentioned, the primary photoproducts of the complexes of BR with human and bovine SA are different: bovine SA does not have a specific effect on the nature of the photochemical transformation of BR, while in the complex with human SA BR undergoes an extremely specific photochemical transformation. Complexes of BR dissolved in the serum of rats suffering from congenital and stimulated jaundice also did not exhibit specific features.

IV. PHOTOTHERAPY OF NEONATAL JAUNDICE AND ITS PROBLEMS

The use of light for the treatment of neonatal jaundice began to be practised after it was observed[63] in 1958 that BR in the serum of a jaundiced infant decomposes in the light. Clinical experiments demonstrating the absence of a neurotoxic effect of the BR photochemical degradation products served as a basis for the practical feasibility of the phototherapy of neonatal jaundice[64,65]. It has also been established[66] that a decrease of the level of BR in the organism during phototherapy is caused not only by the photochemical degradation of BR but also by a change in the nature of the elimination of the undecomposed BR: whereas under the usual conditions BR is eliminated from the organism mainly in a bound state, in phototherapy there is a sharp increase in the amount of unbound BR in the bile, while the elimination of BR in a bound form diminishes. As already mentioned previously, this may be a consequence of the *cis–trans* isomerisation of BR with formation of its water-soluble geometrical isomers[38].

As was to be expected, light in the wavelength range 450–600 nm, corresponding to the BR absorption maximum, exhibits the greatest effect in phototherapy[67]. However, a small effect has also been observed on irradiation with light at a wavelength of ~550 nm and also on ultraviolet irradiation[67].

Despite some contradiction between the results reported by different workers, in most instances successful phototherapy has been achieved by irradiating patients from luminescent sources of blue and white light with a power of 20–40 W, between 3 and 12 of which are placed at a distance of 50–100 cm. More details recommendations concerning the phototherapy of neonatal jaundice are given in a review[68].

The site of the photochemical degradation of the BR molecule on irradiation of a jaundiced infant has not been unambiguously established. Some light has been thrown on this problem by a study[59] of the effect of the shading of individual small (up to ~4 cm^2) sections of the skin in phototherapy. These sections proved to be more pigmented in all cases than the exposed sections of the skin. Hence it follows that BR is firmly retained in the intervascular space and that the "bleaching" effect in phototherapy is due mainly to the decomposition of BR in the surface layers of the skin and not in the vessels. In view of the diffuseness of the boundary line between the shaded and exposed sections of the skin, it was suggested that the effect of light extends along the skin over a distance of ~2 mm. Vogl[69] also claims that BR leaves the vessels more readily than it is able to return to them. It has also been reported[70] that the yellow colour of the skin disappears in the course of phototherapy, while the BR level remains unchanged in the organism. Consequently one may assume that the decomposition of BR in the skin under irradiation is faster than the supply of BR from the blood vessels to the skin.

A group of Indian investigators[71] observed in *in vitro* experiments that the epidermis and skin of man absorbed free and serum-bound BR from an aqueous buffer. After this, the bound BR was readily removed when the skin was transferred to a medium free from BR, while the free BR remained in the skin, imparting a yellow colour to the latter. If the skin was irradiated subsequently with the light from a mercury lamp, then the BR decomposition products accumulated in the medium. Using BR labelled with ^3H, Kapoor et al.[71] established an extremely significant fact: the products for the oxidation of BR absorbed by the skin differ from the products of the oxidation of BR present in the buffer solution. It was suggested that, after emerging from the vessels, BR is bound by the skin lipids and collagen, in which the BR concentration can exceed its concentration in plasma.

The problem of the possible complications in phototherapy has been discussed from the very beginning of its application. In the study of children subjected to phototherapy no arrest was observed in their growth or anomalies in their psychological or physical development[72,73]. Nevertheless, in view of the importance of the problem, special consideration must be given to a number of clinically observed and potential complications.

Complications in phototherapy in which a greyish-brown colouring of the skin, serum, and urine was observed have been reported. This phenomenon may be complicated by anaemia. Cases are known where premature new-born babies, suffering from hyperpigmentation of the skin and subjected to irradiation, showed an arrest of growth[74,75]. An instance of acute haemolysis, accompanying the hyperpigmentation of the skin, on irradiation of a premature infant with daylight lamps has been described[76].

The possibility of the haemolysis of erythrocytes on irradiation in the presence of BR cannot be ruled out. As early as 1932 it was shown[77] that erythrocytes suspended in BR solutions haemolyse on irradiation with sunlight. Subsequently[78] it was suggested that BR is bound to erythrocytes and on irradiation can exert a photodynamic effect on the latter. However, the haemolytic effect of BR can be partly inhibited by proteins[79].

For high doses of irradiation by a luminescent lamp of a suspension of erythrocytes containing BR and at concentrations characteristic of the neonatal period, it was observed[80] that haemolysis is preceded by damage to erythrocyte membranes resulting in the loss of potassium by erythrocytes and a decrease of the activity of ATPase. When BR was introduced into erythrocytes at pH 8 and 10 °C, it sensitised the peroxide oxidation of unsaturated lipids on irradiation with blue light, which was inferred from the positive colour reaction with 2-thiobarbituric acid[81]. The peroxide oxidation of lipids was accompanied by the disappearance of a large proportion of the structural proteins of the membranes and by the appearance of polypeptide photoproducts with a molecular weight in excess of 25000. It was suggested that the photodynamic effect of BR *in vivo* may involve not only erythrocytes but also other cells coming into contact with BR. The photodynamic damage to SA [62] was mentioned above.

Another serious complication in phototherapy may be damage to DNA, which, however, is still one of the problems which have been little investigated. A change in the physicochemical properties of single-stranded DNA *in vitro* has been observed[83] after its irradiation in the presence of BR with light at a wavelength of 450 nm. Bearing in mind the possible relation between the ability to modify cell DNA and the potential mutagenic and/or carcinogenic effect, Speck and Rosenkranz[82] concluded that the possibility of dangerous aftereffects must be completely eliminated in phototherapy.

The appearance of a slight rash, an irritation of the skin, an increase of temperature[77], and an increased loss of water through the skin[83] have been observed in some children on phototherapy. Cases of the tanning of the skin in negro children have been described[84].

In 1974 the National Committee on Phototherapy in the USA suggested in its preliminary report[84] that the phototherapy of neonatal jaundice be regarded as an extremely effective albeit still an experimental method. At the present time most of the large maternity establishments in many countries have already been provided with phototherapeutic apparatus and phototherapy is one of the main methods of preventing the severe and irreversible consequences of neonatal jaundice. Some investigators[85] actually recommend that phototherapy be used as a prophylactic procedure for all new-born infants. However, the majority of investigators nevertheless recommend that phototherapy should be resorted to selectively—only in those cases where the necessity for phototherapy has been firmly established on the basis of the analysis of blood for BR.

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Kinetic Theory of the Flotation of Small Particles

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The present state of the theory of the elementary step in flotation as a multistage process is surveyed. The characteristics of the flotation of small particles both in the stage where they approach the bubble and in the stage involving their fixation to the surface of the bubble are described. It is shown that the deposition of small particles (in contrast to large particles) on the surface of the bubble takes place without inertia and is not accompanied by a significant deformation of the surface. The usefulness of the application of ionogenic surfactants in order to overcome or modify the sign of the disjoining pressure of electrical double layers, which is the commonest factor hindering the flotation of small particles, is demonstrated. The possible ways of intensifying the flotation of submicron particles by their aggregation are analysed.
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I. INTRODUCTION

Until recently the theory of flotation was limited to the thermodynamic consideration of the adhesion of particles to the surface of a bubble, which permitted the analysis of the most important question, from the point of view of enrichment, namely that of the selectivity of the flotation of large particles (with dimensions of ~100 μm and more). The flotation of small particles constitutes an independent scientific problem, because, on transition from coarse to fine grinding, there is a possibility of qualitative changes in the mechanism of the elementary step in flotation (this is understood as the interaction of a single particle with a single bubble).

In the general case one must distinguish in the elementary flotation step the stage involving the approach of the surfaces of the particle and the bubble and the stage in which the particle is fixed on the bubble. In a more detailed treatment it is found that the number of these stages is greater and that the subdivision into stages is itself arbitrary. On passing from large to small particles, the mechanism of the elementary step in flotation is altered both in the approach stage and in the fixation stage. This was first pointed out almost two decades ago[1-10]. At the present time the theory of the elementary step in the flotation of small particles has been developed in a number of investigations[11-22].

II. CHARACTERISTICS OF THE MECHANISM OF THE FIXATION OF SMALL PARTICLES ON THE SURFACE OF THE BUBBLE

The probability of the fixation of a particle is determined by the probabilities of the adhesion of the particle and its retention on the bubble, since in the general case there is a possibility that the initially adhering particle will break away either under the influence of the gravitational force or under the influence of inertial forces. These forces are proportional to the volume of the particles, i.e. are large for large particles and small for fine particles. This trivial fact leads to cardinal consequences in the analysis of the role of particle size in the mechanism of the elementary step in flotation. The forces tending to break away a 100 μm particle are 10^6 times greater than for a 1 μm particle. Therefore for large particles only one form of fixation is possible—via the formation of a three-phase wetting perimeter able to counteract the large forces tending to break it away; we shall henceforth refer to such flotation as contact flotation. For fine particles, there is a possibility, together with contact flotation, also of non-contact flotation, which is not accompanied by the formation of a three-phase wetting perimeter, because for small particles the stripping forces can be balanced by London–van der Waals molecular attraction forces.

Sheludko[23] points to the difficulty of fixing small particles on the surface of a bubble due to the need to overcome the energy barrier to the formation of a three-phase wetting perimeter. One should note that, owing to the Sheludko effect, only contact flotation of small particles may become impossible. The formation of the wetting perimeter is not obligatory for the flotation of small particles; long-range surface forces, in particular the London–van der Waals molecular attraction forces or, what amounts to the same thing, the molecular component of the wedging pressure of the liquid layer separating them are of primary importance. This is the first fundamental difference between the flotation of small particles and the flotation of large particles.

Furthermore, one must take into account the fact that surface forces comprise also the electrostatic interaction forces arising as a result of the overlap of the electrical double layers (DL) of the particle and the bubble, which usually have charges of the same sign[24,25]. The ionic-electrostatic component of the disjoining pressure, due to the interaction of the DL of the bubble and the particle, is an important factor, which can hinder the adhesion of

small particles to the surface of the bubble. This is the second significant characteristic feature of the flotation of small particles. For large particles, the disjoining pressure is overcome by the inertial impact against the bubble surface; for small particles, there is no such impact and the bubble and the particle approach one another without inertia.

The general characteristics of the influence of both components of the disjoining pressure on the fixation of small particles can be established by considering the familiar relation between the interaction energy and the shortest distance between the surfaces of the particle and the bubble which are not in general charged to the same potential[26]. In the case where the bubble and the particle are charged to the same potential and the molecular component of the disjoining pressure is negative, the general theory of the stability and coagulation of lyophobic colloids is applicable[27-30].

In view of the different natures of the bubble and the particle, the condition of the equality of their potentials is attained extremely rarely. It can be observed mainly when the potentials of both the particle and the bubble are so large that the electrostatic component of the disjoining pressure reaches its maximum value. This case is rarely realised; it is possible only in the presence of ionic surfactants, which are capable of imparting a large charge not only to the particle but also to the bubble. Fig. 1*a* illustrates the free energy of the total interaction W of the identically charged particle and the bubble as a function of the distance H between them. This energy is defined by the expression

$$W = a\int_{H}^{\infty} F(H')\,dH' \qquad (1)$$

where F is the force of the interaction described by the familiar formula

$$F(H) = 2\pi a\int_{H}^{\infty} \Pi_e\,dh\ , \qquad (2)$$

where a is the radius of the particle, h the thickness of the plane-parallel layer between the particle and air, $H = h/a$, and Π_e is the electrostatic component of the disjoining pressure.

Eqns. (1) and (2) were derived on the assumption that the particle is a sphere with a radius a, which is much smaller than the radius of the bubble R. Over long and short distances, molecular attraction forces play the main role, while over moderate distances, electrostatic repulsion can predominate. This leads to the formation of an energy barrier separating the near and far potential wells (Fig. 1*a* and 1*b*).

In reality the bubble and the particles differ not only in the surface potentials but also in their behaviour, which can alter qualitatively the interaction arising under these conditions. Thus the case where the potential of the surface of

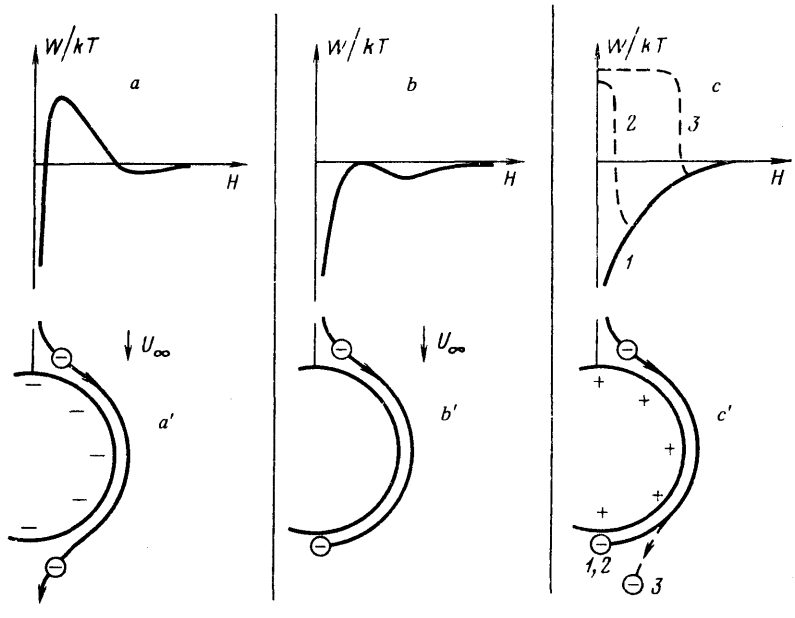


Figure 1. The resultant curves characterising the contribution of molecular attraction forces and electrostatic forces, due to the overlap of the diffuse double layers, to the energy of the interaction W of the bubble and particle at different distances for like surface charges (*a*), on neutralisation of the bubble charge (*b*), and when the bubble charge is altered (*c*, curve *1*). The dashed lines in Fig. 1*c* characterise the contribution of the structural component to the interaction energy over distances shorter (curve *2*) and longer (curve *3*) than the thickness of the double layer. Schemes demonstrating the possibility of flotation for sufficiently large like charges of the particle and bubble (1*a'*), on neutralisation of the bubble charge (*b'*), or on its alteration (*c'*, curve *1*) are shown. Curves *2* and *3* in Fig. 1*c'* illustrate the possibility of flotation for a radius of action of non-electrostatic repulsion forces shorter than the thickness of the double layer (curve *2*) and its impossibility in the opposite case (curve *3*).

the particle and the charge density of the air bubble remain unchanged as h is altered is close to reality. Frumkin[31] and Langmuir[32] showed that, in the special case where the charge of the bubble is zero, a repulsion force arises, which is exactly equal to the repulsion force between two identical particles with a double thickness of the intervening layer. In the light of the theory of heterocoagulation, one should expect that non-inertial flotation is not possible when the bubble and the particles have charges of the same sign, the absolute values of their surface potentials are not small, and the electrolyte concentrations are low (Fig.1*a*). The general theory of heterocoagulation then makes it possible to calculate the potentials (or charges) of the interacting objects for which the electrostatic repulsion force falls so much that the force barrier disappears.

Although the electrostatic repulsion forces persist also when the charge of the bubble is neutralised by the adsorption of surfactants, nevertheless here too the van der Waals attraction forces can predominate and flotation is possible (Fig.1*b*).

Flotation can be ensured by influences of two kinds. When electrolytes are introduced into the system, the thickness of the diffuse component of the double layer diminishes, which leads to a decrease of the electrostatic repulsion forces. The negative surface potential can be reduced by the adsorption of surface-active cations, which also results in coagulation.

The possibility of intensifying the flotation of small particles by lowering the electrostatic repulsion forces was first demonstrated experimentally by Deryagin and Shukakidze[33]. The treatment of the adhesion process in the flotation of small particles on the basis of the heterocoagulation theory, proposed by Deryagin and Dukhin[2], has been described in a series of reviews of the theory of heterocoagulation[34-36]. The importance of reducing the electrostatic repulsion forces for the occurrence of flotation has been proved in recent years in many investigations[37-40]. On varying the electrokinetic potential of silver iodide particles by the adsorption of a cationic surfactant, Jaycock and Ottewill[37] observed a floatability maximum at the isoelectric point. It has been established[37-39] that the rate of flotation is high over a narrow range of pH values and very low outside this range. The above range coincides with the region of very low ζ-potentials of the particle in the vicinity of its isoelectric point. The addition of aluminium hydroxide extends the pH range favouring flotation.

The authors of the above studies interpreted their data as evidence for the decisive influence of the electrostatic component of the disjoining pressure on the adhesion of particles to the bubble. Collins and Jameson[40] assumed in addition the possibility of another interpretation of the results. The disappearance of the electrostatic repulsion force barrier can cause intense coagulation of particles at the isoelectric point. The aggregates thus arising can be more rapidly precipitated on the surface of the bubble than single particles. In order to rule out this possibility, the authors[40] measured the change in the distribution of spherical polystyrene particles 4–20 μm in size, in the flotation process at different electrolyte concentrations and correspondingly for different electrophoretic mobilities of the particles, i.e. for different values of the electrokinetic potential. For each of the eight fractions investigated separately, the rate of flotation increased monotonically with decrease of the ζ-potential of the particles and bubbles. Since these experiments made it possible to follow the influence of both the size and the charge of the particles separately on flotation, the necessity for eliminating the disjoining pressure of the double layers as an essential condition for flotation was demonstrated unambiguously by the above investigators†.

The special introduction of electrolytes in order to ensure floatability is naturally not technologically viable. A more economical method of controlling the electrostatic component of the disjoining pressure and hence the floatability consists in the use of ionogenic surfactants at specific concentrations whose adsorption on the bubble causes a change in its charge. However, very low surfactant concentrations do not ensure floatability if the latter is hindered not only by the electrostatic barrier but also by non-electrostatic factors preventing the mutual approach of the surfaces of the particle and the bubble. One of such factors may be the presence on the surface of the particle of a polymolecular hydrate layer. The possibility of the existence of a polymolecular hydrate layer, preventing a decrease in the thickness of the wetting films as a result of the structural component of the disjoining pressure, on lyophilic surfaces has been established by a number of investigators[41-43].

The barrier due to the structural component of the disjoining pressure is illustrated schematically in Fig.1*b* for those cases where its radius of action is smaller (curve *2*) or greater (curve *3*) than the thickness of the double layer. One of the ways of ensuring or improving floatability in the presence of the structural component consists in employing surfactants whose adsorption renders the surface of the particle hydrophobic, or destroys the structural component of the disjoining pressure, or alters its sign.

Another way of overcoming the difficulty associated with ensuring the flotation of dispersions in the presence of a non-electrostatic factor stabilising colloids has been indicated by Deryagin and Dukhin[2]; it consists in stimulating electrostatic attraction. For this purpose, it is necessary to generate, by means of a high degree of adsorption of surfactants, a high charge on the surface of the bubble opposite in sign to that of the particle; the interaction between the double layers then ensures the operation of attraction forces. If the thickness of the double layer exceeds that of the hydration layer, then, outside the limits of the radius of action of non-electrostatic repulsion forces, attraction forces will operate between the opposite charges of the particle and the bubble. Thus an aggregate comprising the bubble and the particle, between the surfaces of which there is a gap of the order of magnitude of the thickness of the non-electrostatic repulsion force barrier, is produced. If the radius of action of the repulsion forces is increased for the same double layer thickness, then the potential well becomes smaller. It is desirable to select surfactants in such a way that not only the electrostatic attraction is increased but also the repulsion due to the structural factor is reduced. Thus, if the radius of action of electrostatic attraction forces exceeds that of the non-electrostatic repulsion forces (of structural origin), floatability is possible (Fig.1*c*, curves *2*). If the radii of action of these forces are comparable, then in the presence of the non-electrostatic barrier flotation proves to be impossible (Fig.1*c*, curves *3*).

Thus the third characteristic of the flotation of small particles consists in the fact that it can be controlled with the aid of ionogenic surfactants and it is possible to ensure floatability even when non-electrostatic stability factors operate. This conclusion is confirmed by the available experimental literature data. Thus it has been shown[44] that the surface not only of pure but also of methylated

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†The possibility of the aggregation of particles was ruled out by sufficiently high values of their ζ-potentials.

quartz has hydrophilic sections which ensure the stability of suspensions and hinder flotation. The floatability of quartz has been ensured[45] in the range of dodecylammonium chloride concentrations in which the surface charges of the bubble and the particle have opposite signs.

Systematic studies by Schulze[46,47] have shown that the water–air and water–quartz interfacial films become unstable under the influence of the adsorption of tervalent cations or cationic surfactants if their thickness is smaller than a critical value h_{cr}. The critical thicknesses are 300–450 Å under conditions where the surface of quartz is altered by tervalent cations. The change in the charge of the bubble surface by the adsorption of cationic surfactants leads to the rupture of the film for thicknesses of 150 Å if the electrolyte concentration is high and for thicknesses of 1500 Å if it is low, which agrees with the electrical nature of the attraction arising under these conditions. Schulze also suggests that floatability be increased by altering the surface charge of the bubble as a result of the adsorption of surfactants at the lowest possible electrolyte concentration, which should increase the thickness of the double layer and hence h_{cr}.

The above conclusions by Schulze agree with the data of Goddard and coworkers[48], who ensured the flotation of quartz particles by the adsorption modification of the surface charge of the bubble using amines. A sharp increase in floatability corresponds to a sharp increase in the degree of adsorption of amines. Whereas floatability is usually controlled by rendering the surface of the particle hydrophobic, in the present instance we are dealing with a completely new trend in flotation, where the surface charge of the bubble is modified by introducing a surfactant. The insignificant changes in the surface of quartz are indicated by the fact that in Goddard's experiments the ζ-potential of quartz changed very little after the introduction of the surfactant.

The depth of the potential well arising outside the limits of the non-electrostatic barrier when the surface of the bubble is altered is insufficient for the contact-free flotation of large particles. The contact-free flotation of particles in the presence of the non-electrostatic component of the disjoining pressure can therefore be ensured by altering the charge of only fairly small particles.

III. CHARACTERISTICS OF THE MECHANISM OF THE TRANSFER OF SMALL PARTICLES TO THE SURFACE OF THE BUBBLE

The approach of the particle to the surface of the bubble undergoes qualitative changes on passing from long (compared with the particle size) distances between their surfaces to short distances. Over long distances, the above process is determined by the operation of only two factors—inertial forces and hydrodynamic interaction. Under the influence of inertial forces, a fairly large particle moves almost linearly until its collision with the surface of the bubble, which occurs if $b < R + a$ (Fig.2). The stream of liquid flows around the surface of the bubble, the flow lines of the liquid are curved, and the particle is involved in this movement in one way or another. The smaller the particle size and the smaller the difference between its density and that of the medium, the smaller the inertial forces acting on it and the closer the agreement between its trajectory and the flow lines of the liquid. Thus, for the same target distance, large particles move along virtually straight lines (Fig.2, line *1*), whereas the trajectories of small particles virtually coincide with the corresponding flow lines of the liquid (line *2*). The trajectories of particles of intermediate size are distributed in the region bounded by lines *1* and *2* and, with decrease of particle size, they shift from line *1* to line *2* and the possibility of collision diminishes.

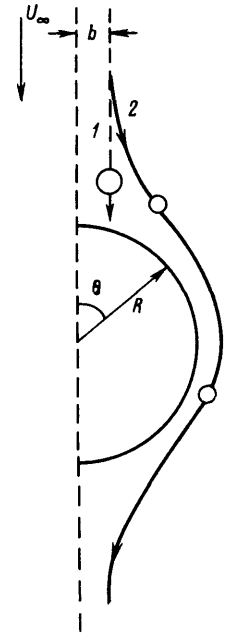


Figure 2. The influence of the inertia of the particles on their trajectories in the vicinity of a rising bubble. The trajectories of large (inertial, line *1*) and small (non-inertial, line *2*) particles for the same target distance *b* are shown.

The deviation of the trajectories of small particles from the linear path towards the surface of the bubble over distances of the order of magnitude of the size of the bubble is caused by a hydrodynamic effect, which can be naturally referred to as a long-range effect. The bubble curves the flow lines of the liquid and thereby curves the trajectories of small particles, i.e. acts on them via the velocity field of the liquid. For large particles, inertial forces greatly exceed the long-range hydrodynamic interaction (LHI) forces and such interaction therefore has only weak effects. On the other hand, for small particles, the inertial forces are small compared with LHI forces[1]. Thus the approach of large particles to the bubble is ensured by inertial forces, whereas in the case of small particles the process is non-inertial and is greatly hindered by the long-range hydrodynamic interaction. This constitutes the first difference in the transport of small particles to the surface of the bubble.

Together with the long-range hydrodynamic interaction, in which the trajectory of the non-inertial movement of the particle coincides with the flow line of the liquid, there exists a hydrodynamic interaction over distances of the order of magnitude of the radius of the particle. The latter leads to the deviation of the particle trajectories from the corresponding flow lines of the liquid. It is natural to refer to such interaction as the short-range hydrodynamic

interaction (SHI). On the basis of Taylor's solution of the hydrodynamic problem of the displacement of liquid from the gap as a spherical particle approaches a planar surface, it has been shown[2] that the SHI can prevent contact between the particle and the bubble. According to Taylor, for a gap thickness $h \ll a$, the hydrodynamic resistance of the film to a decrease of its thickness is given by

$$f = va/h \ , \qquad (3)$$

where v is the rate of approach of the particles to a section of the bubble surface which can be regarded by convention as planar. If the particle is acted upon by a constant adhesional force F, then according to Eqn.(3), we have

$$v \propto Fh/a \ . \qquad (4)$$

Hence it follows that, for the complete removal of the liquid from the gap, an infinitely long time is required:

$$T = \int_h^0 \frac{dh}{Fh} = \frac{1}{F} \ln h \Big|_h^0 \to \infty \ . \qquad (5)$$

The problem therefore arises of the nature of the forces adhering the particle to the surface of the bubble. This paradox is removed if account is taken of the action of the surface attraction forces arising with decrease of the distance faster than the viscous resistance of the film. The decrease of the thickness of the latter for thicknesses of the order of magnitude of the effective radius of action of the surface forces occurs under the influence of the adhesional hydrodynamic force. Above the equatorial plane, the flow lines of the liquid approach the surface of the bubble. This implies that the radial component of the velocity of the liquid is directed to the surface of the bubble. Since in the SHI zone the movement of the particles to the surface is hindered, the radial component of the velocity of the liquid is greater than the radial component of the velocity of the particle and for small gaps and correspondingly for a high viscous resistance it is much greater. As a result the radial flow of the liquid around the particle, which retards its approach to the bubble, clamps it to the bubble. To a first approximation, this hydrodynamic force can be estimated from the Stokes formula by substituting in the latter the radius of the particle and the difference between the local velocities of the liquid and the particle.

Thus the decrease of the thickness of the interfacial film in the case of large particles takes place as a result of inertial impact, while in the case of small particles it is caused by the adhesional hydrodynamic force, which constitutes yet another significant difference characteristic of the flotation of small particles.

The decrease of the thickness of the interfacial film is complicated for large particles by the presence of a dent arising on the surface of the bubble following the inertial impact by the particle. It has been shown[22] that, in the non-inertial deposition of small particles on the surface of the bubble, the deformation of the latter under the influence of the adhesional hydrodynamic force is insignificant. This third considerable difference facilitates the derivation of a quantitative kinetic theory of the flotation of small particles.

IV. A QUANTITATIVE THEORY OF THE FLOTATION OF SPHERICAL PARTICLES OF SMALL AND MODERATE SIZES

The approach of the particles to the surface of the bubble can be described quantitatively by taking into account both the long-range and the short-range hydrodynamic interactions. In order to estimate the efficiency of flotation, we introduce the dimensionless parameter E, given by

$$E = b_{cr}^2/R^2 \ , \qquad (6)$$

where R is the radius of the bubble and b_{cr} the maximum radius of the tube of streaming liquid incident on the bubble, in which all the particles are deposited on the surface of the bubble (Fig.3). The particles moving along a flow line with a target distance $b < b_{cr}$ are deposited on the surface of the bubble (Fig.3, curve *2*); otherwise the particle is carried away by the stream. Fig.3 shows that the calculation reduces to the evaluation of the so-called "limiting trajectory" (Fig.3, curve *1*) and hence of the target distance b_{cr}.#

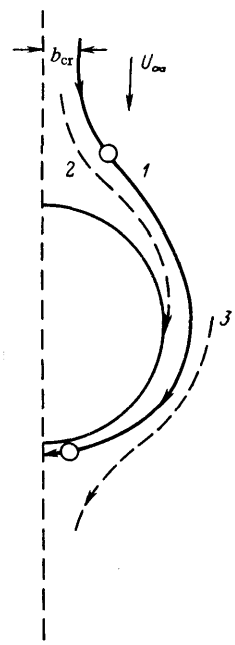


Figure 3. Illustration explaining the concept of the limiting particle trajectory (curve *1*). The trajectories of particles for $b < b_{cr}$ (curve *2*) and $b > b_{cr}$ (curve *3*) are shown by dashed lines.

The flow of liquid around a rising bubble is of the potential type if the movement of its surface is not retarded by the influence of a surfactant and the Reynolds number

$$\mathrm{Re} = \frac{2RU_\infty}{\nu} \qquad (7)$$

greatly exceeds unity (U_∞ is the rate at which the bubble rises and ν is the kinetic viscosity of the medium). If account is taken of the quadratic relation between the velocity of the bubble and its radius, it is easily seen that the Reynolds number varies very rapidly with the radius.

#An analogous approach is used in the theory of aerosols[49].

This number is unity for $R \cong 80$ μm. The concept of the length of the inertial path of the particle l, i.e. the distance which the particle can traverse, despite the viscous resistance of the liquid, as a result of its initial velocity

$$l = \frac{2}{9}\frac{U_\infty a^2 \rho'}{\eta} , \qquad (8)$$

where ρ' is the difference between the densities of the particles and the medium and η is the viscosity of the medium, is important for the understanding of the mechanism of the inertial deposition of particles on a rising bubble.

The normal component of the velocity of the liquid on the surface is zero; the thickness of the layer of liquid in which this component decreases as the surface is approached is of the order of magnitude of the radius of the bubble. The particles traverse this layer of liquid because it falls within the limits of their inertial path. Hence it is clear that the possibility of the inertial deposition of the particle depends on a dimensionless parameter of the type

$$\lambda = l/R . \qquad (9)$$

For $\lambda > 1$, deposition is evidently possible. However, calculations showed that it is possible also for $\lambda < 1$ provided that λ is not too small. This can be understood if account is taken of the fact that a particle in a layer with a thickness R moves to the surface not only as a result of inertia but also together with the liquid. Inertial deposition is impossible if λ is smaller than a critical value λ_{cr}. Under the condition of a potential regime in the flow of liquid around the bubble and when the particle size is neglected, calculation yields the following result[50]:

$$\lambda_{cr} = {}^1/_{2\lambda} . \qquad (10)$$

Using Eqns.(8) and (9), it is easy to obtain a formula for the critical radius of the particle, below which inertial forces do not ensure the approach of the particle to the bubble:

$$a_{cr} = \frac{9}{\sqrt{48}}\sqrt{\frac{\nu\eta}{9\rho' g R}} \simeq 4 \cdot 10^{-1} R^{-1/2} \qquad (11)$$

where g is the acceleration due to gravity.

For $a > a_{cr}$, the inertial deposition of the particles on the surface of the bubble takes place, but its intensity diminishes with decrease of a. This is reflected in the formula for the efficiency of the collision, obtained initially in relation to the coagulation of aerosols[49] and then extended[2] to the elementary step in flotation:

$$E = \frac{\lambda^2}{(\lambda + 0.5)^2} . \qquad (12)$$

This formula has been recently confirmed[52] in the range $\lambda = 0.07-3.5$.

In the light of the studies described above, it is convenient to introduce the subdivision of particles into large, medium, and small. Particles for which E, calculated by Eqn.(12), is close to unity can be regarded as "large". Particles with $a < a_{cr}$ can be naturally referred to as "small", while "medium" particles are those for which inertial deposition is possible but the collision efficiency is less than unity.

As will be seen from what is to follow, in the non-inertial approach of particles to the surface of the bubble, the intrinsic size of the latter plays an important role. The closest approach of the flow lines of the liquid to the surface of the bubble is attained in the equatorial plane. Fig.4 illustrates schematically by a dashed line the flow line of the liquid (curve *1*) whose distance from the surface of the bubble in the equatorial plane is equal to the radius of the particle. Some workers believe erroneously that this is the limiting flow line for particles of this radius, the error consisting in the fact that one does not then take into account the SHI. Under the influence of the SHI the particle is displaced from this flow line of the liquid, since its trajectory (curve *2*) in the equatorial plane is separated from the surface by a distance exceeding the radius. There is therefore no contact with the surface and hence b is not the critical target distance. Bearing in mind that, owing to the SHI, the distance of the particle from the surface in the equatorial plane is greater than the distance along the flow line, with which the particle trajectory coincides over longer distances from the bubble, one may conclude that $b_{cr} < b(a)$. A characteristic feature of the limiting flow line (curve *3*) is that the particle trajectory branching away from it under the influence of the SHI (curve *4*) passes at a distance a from the surface of the bubble in the equatorial plane.

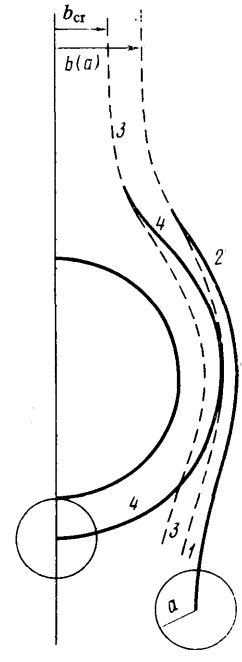


Figure 4. The influence of particle size in non-inertial flotation on their trajectories in the vicinity of the rising bubble. The flow lines in the liquid, corresponding to the target distances b (a) and b_{cr}, are shown dashed. The continuous lines characterise the deviation of the particle trajectories from the flow lines of the liquid under the influence of SHI.

Thus b_{cr} diminishes, firstly, as a result of the deviation of the flow lines of the liquid and the influence of the LHI and, secondly, as a result of the deviation of the particle trajectory from the flow line under the influence of the SHI. The efficiency of the collision is therefore expressed by the product of two factors, E_0 and f, each of which is less than unity; the former expresses the influence of the LHI and the latter that of the SHI.

In the potential flow regime the following expression holds[53]:

$$E_{0p}=3a/R_p \qquad (13)$$

where the subscript p corresponds to the potential regime in the flow around the bubble. For Re < 1, the flow of liquid becomes viscous. The movement of the surface of the bubble is then usually fully retarded by the absorption layer of surfactant, so that the distribution of velocities is then described by the Stokes formula. Furthermore, according to Okazaki[54], for Re < 20 the bubble rises like a solid sphere also in the absence of surfactants. An analogous formula for Stokes regime, which we shall denote by subscript s, is§

$$E_{0s}=\frac{3}{2}\left(\frac{a}{R_s}\right)^2 , \qquad (14)$$

The problem of the adhesional hydrodynamic force, favouring a decrease of the thickness of the interfacial film in the SHI, has been solved for the Stokes regime[56] and for the potential regime[19]. It was established that the adhesional force is 2–3 times greater than the value calculated from the Stokes formula. The adhesional hydrodynamic force cannot ensure contact between the particle and the bubble, since it has a finite value and the resistance increases infinitely as the thickness of the interfacial film diminishes.

It has been shown[2] that non-inertial flotation is possible by virtue of the operation of surface forces. Here there is a possibility of two cases. It is known[57,58] that interfacial films can lose their stability and can be disrupted spontaneously when a critical thickness h_{cr} is reached as the thickness diminishes. On replacing zero by h_{cr} in the integration limits in Eqn.(5), we obtain as a result of integration $\ln(h_0/h_{cr})$ instead of infinity. Thus non-inertial flotation is possible in the presence of flotation agents ensuring the validity of the condition $h_{cr} \neq 0$.

The molecular force of the interaction between a spherical particle and a planar surface is given by the following formula[59] for a sufficiently small value of h:

$$F=Aa/6h^2 , \qquad (15)$$

where A is the Hamaker constant. Since the attractive force defined by Eqn.(15) increases with decrease of h faster than the resistance force of the viscous layer, contact leads to the rupture of the layer. The influence of the SHI on the efficiency of the capture of the particle has been calculated[11,12] for $h_{cr} \neq 0$ neglecting the long-range molecular forces. The formulae obtained using the Stokes and potential distributions of velocities are

$$E_s=E_{0s}f_s , \qquad (16)$$

$$E_p=E_{0p}f_p , \qquad (17)$$

where f_S and f_p are functions reflecting the influence of the SHI on the elementary step in flotation. For any value of the dimensionless parameter $H_{cr} = h_{cr}/a$, these functions are less than unity, decrease with decrease of H_{cr}, and become zero when $H_{cr} = 0$, which agrees with the hypothesis concerning the mechanism of the influence of the SHI on the deposition of the particles described above. With decrease of H_{cr} from 10^{-1} to 10^{-3}, the function f_S diminishes from 0.5 to 0.15, i.e. the dependence of E_S on the absolute value of h_{cr} is very weak. Thus SHI can be taken into account only when one considers the question of the possibility of flotation; this effect diminishes severalfold the number of steps in which the particles come into contact with the bubble.

The SHI theory has been developed[13] without using the phenomenological parameter h_{cr} by allowing directly for the dependence of the molecular forces on h. The following expressions were then obtained:

$$E_s = E_{0s}f_s(w_s);\ w_s=\frac{2AR_s^4}{27U_s\pi\eta a^4} ; \qquad (18)$$

$$E_p = E_{0p}f_p(w_p);\ w_p=\frac{4AR_p}{27U_p\pi\eta a^3} , \qquad (19)$$

where U_S and U_p are the rates at which the bubble rises in the Stokes and potential regimes. Numerical analysis of the universal functions f_S and f_p made it possible to approximate Eqns.(18) and (19) (in the CGS system) as follows:

$$E_s \simeq 0.11\frac{a^{1.4}}{R_s^2}A^{1/6} , \qquad (20)$$

$$E_p \simeq 1.1\frac{a^{0.8}}{R_p}A^{1/1.8} . \qquad (21)$$

Although the absolute value of E depends very slightly on the Hamaker constant, whose value is in the range from 10^{-14} to 10^{-12} erg, nevertheless flotation is impossible for $A < 0$, i.e. when the dispersion force is directed away from this surface of the bubble. Thus molecular forces act almost in accordance with the "yes or no" principle depending on the sign of A.

The adhesional hydrodynamic force can exceed the force barrier due to the disjoining pressure and hence can ensure the possibility of reagent-free flotation. This question can be investigated by considering the movement of the particle along the symmetry axis of the bubble from the side of the advancing stream of liquid[60]. Since the adhesional force is a maximum under this condition, it is possible to obtain the necessary and sufficient condition for the deposition of particles on the surface of the rising bubble.

Along the bubble axis, the tangential flow rate of the liquid is zero, so that the deposition process can take place over an infinitely long period. However, this implies that the viscous resistance of the interfacial film can then be infinitely small and can be neglected in the balance of the acting forces[60]:

$$F(h, a)=F_V+F_E+F_H+F_G , \qquad (22)$$

where F_V is the adhesional hydrodynamic force, F_H the molecular force of attraction, F_E the electrostatic force, and F_G the gravitational force. Condition (22) implies that a force directed towards the surface (to the upper pole) of the bubble should act on the particle for any h, since otherwise deposition is impossible. Condition (22) sets limits to the parameters in the formulae for the four forces at which the "disjoining" pressure can be overcome. These limits are illustrated graphically in Figs.5 and 6 by curves characterising the dependence of the particle radius on the electrolyte concentration and covering the region close to the original of coordinates, where flotation is impossible. The regions of floatability due to the adhesional hydrodynamic force have been calculated for the Stokes (Fig.5) and potential (Fig.6) regimes in the rise of the bubble. As was to be expected, flotation is possible also appreciably below the heterocoagulation theshold when the particle size is not unduly small. In the potential regime, the adhesional

§ Eqn.(14) was apparently first obtained[1] by analogy with the mechanics of aerosols. Eqn.(14), revised by taking into account the gravitational component, has been derived by Reay and Ratcliff[55].

hydrodynamic force is much greater than in the Stokes regime, as a result of which flotation becomes possible for larger electrostatic attraction forces or smaller particles sizes.

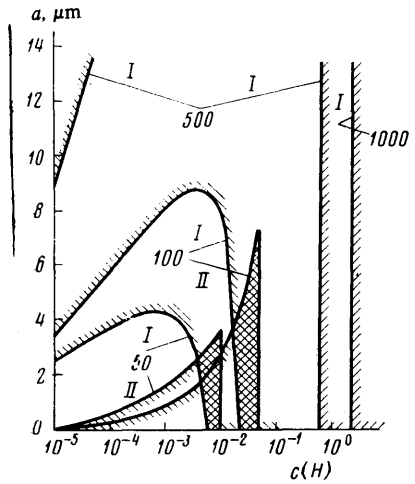


Figure 5. The $a - c$ regions illustrating the floatability in the Stokes regime (shown dashed): I) the lower limit of flotation at the primary minimum; II) the upper limit of flotation at the secondary minimum; 50, 100, 500, and 1000—numerical values of the product $\psi_a\psi_R$ expressed in mV^2. The following quantities are expressed in CGS units: $A = 5 \times 10^{-14}$, $\varepsilon = 80$, $g = 10^3$, and $\rho_{particle} = \rho_{water} = 1$.[60]

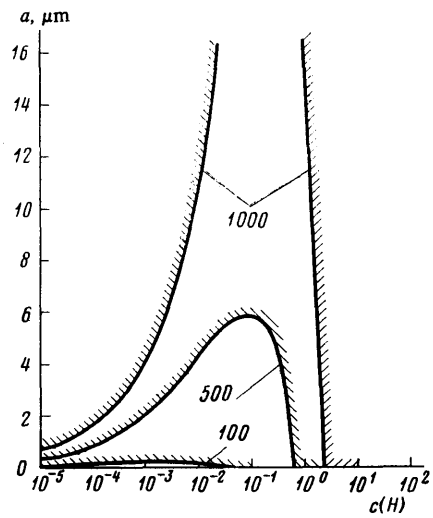


Figure 6. The a–c regions of floatability in the potential regime (shown dashed); 100, 500, and 1000—numerical values of the product $\psi_a\psi_R$ expressed in mV^2. The following quantities are expressed in CGS units: $A = 5 \times 10^{-14}$, $\varepsilon = 80$, $R = 2.5$, $\eta = 10^{-2}$, and $U_r = 15$.[60]

Flotation without overcoming the barrier is difficult owing to the breaking away of the particles at the lower pole of the bubble. The component of the flow rate of the liquid at the upper pole, at right angles to the bubble surface, is responsible for the force adhering the particle to the surface, while that at the lower pole is responsible for the force tending to break it away. Consequently the stripping force differs from the adhesional force only in sign. Therefore the possibility of the fixation of the particles at the secondary energy minimum[30] can be analysed also with the aid of condition (22). Since the stripping force diminishes with particle size, flotation via the fixation of the particles at the secondary minimum proves to be possible for sufficiently small particles. Therefore curve II in Fig.5 sets the upper limit to the size of the particles undergoing flotation. In view of the increasing stripping force, in the potential regime the fixation at the secondary minimum is possible only for very small particles, for which the effect is complicated by thermal movement.

Thus a quantitative description of non-inertial flotation has been given at the present time only in two limiting cases—for sufficiently small and sufficiently large values of the product of the Stern potentials of the particle (ψ_a) and the bubble (ψ_R). In the former case electrostatic interaction does not complicate flotation and Eqns.(20) and (21) can be used; in the latter case flotation is impossible¶.

Since the electrical double layer is compressed with increasing electrolyte concentration and the parameter $\psi_a\psi_R$ decreases, in the light of the data presented in Fig.6 one should expect the possibility of the reagent-free flotation of small particles below the heterocoagulation threshold but at a fairly high concentration of the electrolyte (naturally provided that there are no non-electrostatic stability factors). The significant differences in the Stokes and potential regimes both in the LHI and in the process involving the overcoming of the disjoining pressure already discussed demonstrate the importance of an adequate description of the hydrodynamic field surrounding the bubble in the elementary flotation step. It is useful to employ the hydrodynamic field calculated[62,63] for intermediate values of Re. A formula has been obtained[61] for E [analogous to Eqn.(14)] for conditions under which the hydrodynamic field described by Hamielec and coworkers[62,63] is applicable and the surface of the bubble is stationary.

Within the framework of the general consideration of the equation for particle trajectories, it has been shown[1] that the sedimentation of particles has very little influence on their capture by the bubble, provided that its probability is sufficiently high, so that condition (7) does not hold. For this reason, Deryagin and Dukhin[2] disregarded the sedimentation term in the equation for the particle trajectories. Flint and Howarth[64] regard the force of gravity as the most important factor influencing the capture of small particles by bubbles of any size and object to the neglect of sedimentation, as was done by Deryagin and Dukhin[2,5]. According to Flint and Howarth[64], the quantity E_0 is proportional to the difference between the densities of the particle and the medium ρ' or more precisely to the dimensionless parameter $G = 2\rho' a^2 g/9\eta U_\infty$. However, this implies that, when the densities of the particle and the

¶In the course of the preparation of this review for the press, the paper by Rulev et al.[97] was published in which the kinetic theory of the flotation of small particles was extended to the case of arbitrary values of ψ_a and ψ_R and a quantitative interpretation of the experimental data of Rulev et al.[15] was given.

medium are equal, i.e. when $\rho' = 0$, non-inertial flotation is impossible. This conflicts particularly with Sutherland's equation (13) in which the difference ρ' is not included at all. This conflict arose because Flint and Howarth did not take into account the most important factor in the non-inertial flotation of small particles, namely their finite size.

Anfruns and Kitchener[61] disregarded the finite particle size and Sutherland[53] disregarded the force of gravity. It is easy to take these factors into account simultaneously and to compare their influences on this basis. The functions characterising the particle trajectories in the studies of the above investigators[53,61] differ only by the fact that Anfruns and Kitchener took into account the influence of sedimentation. We shall therefore use the more general formula [Eqn.(6)] of Anfruns and Kitchener[61] describing the family of particle trajectories:

$$\Psi_p^* = \frac{1}{2}\sin^2\theta\left[r^2\left(1 + G - \frac{1}{r^3}\right)\right].$$

Anfruns and Kitchener[61] isolate the limiting trajectory from the entire family of trajectories by taking into account the following condition: $r = 1$ when $\theta = \pi/2$. If this condition is refined by allowing for the finite particle radius ($r = 1 + a/R$ when $\theta = \pi/2$), then the following more general and more accurate formula is obtained:

$$E_0 = \frac{(1+G)\,E_p + G}{1+G} \quad . \qquad (23)$$

If the force of gravity is neglected (we than have $G = 0$), Sutherland's formula is obtained from Eqn.(23). If the finite particle size is neglected, i.e. if we put $E_p = 3a/R = 0$, the equation of Flint and Howarth[64] is obtained.

In the hydrodynamic theory of flotation no account is taken at the present time of the influence of the particle on the hydrodynamic field of the bubble, i.e. the ratio a/R plays the role of a small parameter. The factor G, proportional to $(a/R)^2$, is therefore a small second-order quantity, while the factor E_p, proportional to (a/R) [Eqn.(13)], is a small first-order quantity. The quantity G in Eqn.(23) can therefore be neglected and the equation is transformed into Sutherland's formula also when the force of gravity is neglected. Thus, under the conditions of potential flow, the force of gravity does not influence the kinetics of non-inertial flotation and the conclusions of Flint and Howarth[64] are incorrect.

At the same time one must introduce the correction that, with decrease of the size of the bubble and particularly with increase of the retardation of the movement of its surface, the influence of the sedimentation of particles on the flotation kinetics increases. For example, the allowance for the force of gravity on the kinetics of the flotation by bubbles rising in the Stokes regime, carried out by Reay and Ratcliff[55], is quite appropriate. This is consistent with the finding that in this instance E_{0S} and G are of comparable order of magnitude, as can be seen from Eqn.(14).

V. QUANTITATIVE EXPERIMENTAL STUDIES OF THE FLOTATION OF SMALL PARTICLES

In recent years considerable advances have been made in the experimental study of the influence of the sizes of the bubble and spherical particles on the collision efficiency in the Stokes regime[40,65]. A study has also been made of the flotation[15] of a petroleum emulsion by bubbles whose size ensures a close approach to the potential regime. In satisfactory agreement with Eqn.(21), it was then established that $E_p \propto a$. Studies by Deryagin and coworkers[9,10] confirmed the marked influence of the LHI in non-inertial flotation. Its most important manifestations, observed experimentally, are a rapid decrease of E with decreasing particle size and increasing bubble size and also a sharp alteration of the nature of the dependence of E on R and a on passing from the viscous to the potential flow regime. It must be emphasised that Eqn.(20) is in quantitative agreement with the data of Collins and Jameson[40] and Reay and Ratcliff[65] in relation to the dependence both on the particle size and on the radius of the bubble. The experimental finding that $E \propto a^{1.5}$ implies a better agreement with Eqn.(20) than with Eqn.(14). This can be regarded as experimental confirmation of the influence of the SHI on the elementary step in flotation. However, one must recognise that there have been no systematic experimental studies of the SHI at the present time.

Studies of the efficiency of capture by single bubbles 0.5–1.1 mm in diameter of several fractions of quartz which has been rendered hydrophobic (methylated), confirmed[61] the formula taking into account only the long-range hydrodynamic interaction. The authors[61] therefore concluded that the disjoining pressure of the double layers does not complicate the flotation step at least under the conditions of their experiment. An analogous conclusion could be formulated in relation to the SHI.

However, these conclusions cannot be regarded as firmly justified, since it is possible to propose a different interpretation of these interesting experimental data. This other possibility is associated with the fact that the theory of the SHI and of the influence of the double layer on flotation has been developed for spherical particles, while Anfruns and Kitchener[61] investigated non-spherical particles—fragmented Brazilian quartz. One must therefore postulate the existence of edges separating the faces on the surface of such particles. The resistance to the decrease of the thickness of the interfacial film can be much more readily overcome if the angles between the faces (or between the edges) are sufficiently small, so that the interfacial film can be "pierced" by the sharpened section of the particle surface. Similar geometrical conditions in the elementary step in flotation sharply facilitates also the overcoming of the disjoining pressure. The surface microrelief cannot have a strong influence on the LHI, since Eqns.(13) and (14) and the formula of Anfruns and Kitchener[61], which have been derived for spherical particles, remain in force also as an approximation for non-spherical particles.

In the light of the foregoing and the results of Anfruns and Kitchener, the formulation of the theory of the flotation of small particles has been significantly revised: the characteristics of the influence of the SHI and of surface forces on the elementary step in flotation can differ sharply in relation to spherical and non-spherical particles and must therefore be investigated separately. The deviation of the shape of the particle from the spherical can not only reduce but can also greatly increase the role of the SHI and of the double layer in flotation. The decrease of the thickness of the plane-parallel interfacial film between the bubble and a lamellar particle is even slower than for a spherical particle, so that the role of the SHI sharply increases in this instance. This is to be expected for a thin lamellar particle. On the other hand, if the particle is not thin, one may expect that its migration along the surface of the bubble is accompanied by rocking. In the course of rocking, orientations of the particle relative to the bubble surface arise in which the viscous resistance of the interfacial film and the disjoining pressure of the double layer are overcome so rapidly that the

SHI has only slight influence on E.†

VI. THE BREAKING AWAY OF SMALL PARTICLES IN CONTACT-FREE FLOTATION AND THE DYNAMIC ADSORPTION LAYER OF THE BUBBLE

If flotation is uncomplicated by energy barriers and $h_{cr} \neq 0$, then the approach of the particles terminates with the rupture of the film and the establishment of a wetting angle so that the possibility of breaking away is ruled out under these conditions.

If the double layer does not complicate flotation but there is a non-electrostatic barrier with a thickness h_0, then the possibility of the particle breaking away can be estimated as in the study of Deryagin et al.[60], where the possibility of coagulation at the secondary minimum in flotation was examined (Fig.5). For this purpose, it is sufficient to consider the condition of the equality of the sum of the hydrodynamic and gravitational stripping forces to the molecular attraction force at $h = h_0$ at the lower pole of the bubble. This leads to the following estimate of the particle radius a_{max} below which contact-free flotation is possible in the Stokes regime (in the CGS system):

$$a_{max} = 3 \cdot 10^{-3} \frac{\sqrt{A}}{h_0} \quad . \qquad (23')$$

If it is assumed that A varies in the range 10^{-14}–10^{-13} erg and h_0 varies in the range 10–100 Å, then a_{max} is in the range 3–100 μm. Thus difficulties for contact-free flotation arise when the Hamaker constant A is small or the thickness of the barrier h_0 is large. In this situation the opposite charges of the particle and the bubble must be achieved by introducing an ionogenic surfactant in order to ensure contact-free flotation. This is possible for a greater thickness of the barrier the lower the electrolyte concentration.

By overcoming the disjoining pressure of the double layer via the adhesional hydrodynamic force (Figs.5 and 6), one guarantees that the particle, which has migrated to the lower pole of the bubble, cannot break away only when the depth of the primary (near) potential energy minimum is sufficiently great. It has been shown[65,67,68] that after coagulation subsequent breakdown of the resulting aggregate is possible, since the depth of the primary minimum may be small. Coagulation at the primary minimum does not occur or is reversible with increase of concentration in the range characteristic of the coagulation of lyophobic colloids if the Stern potential is fairly high and the depth of the well is small. The question of the depth of the primary minimum is very complex. In the case of flotation it is complicated still further in view of the lack of information about the charge of the bubble.

Since the question raised in connection with the study described in Refs.65–68 is far from solved, we shall confine ourselves to a single general remark. The depth of the primary potential well decreases with increasing charge of the interacting surfaces. Therefore the smaller the product $\psi_a \psi_R$, involved in the theory of heterocoagulation (Figs.5 and 6), the smaller is the probability that the particles which had previously overcome the disjoining pressure of the double layer via the adhesional hydrodynamic force will break away. The greater the value of this product, the smaller the depth of the primary potential well, and the greater the probability that the particles will break away (particularly if the Hamaker constant is small). In other words, the condition for overcoming the disjoining pressure via the adhesional hydrodynamic force for sufficiently low values of the product $\psi_a \psi_R$ is necessary and sufficient for flotation. For higher values of this product, the above condition becomes only necessary.

The possibility of breaking away increases with increasing size and the rising velocity of the bubble. The mechanism of the stripping process can then be complicated by the deformation of the double layer on the mobile bubble surface, which can lead to an increase of the surface charge and hence of the electrostatic repulsion forces at the lower pole of the bubble. When the size of the bubble is not unduly small, its surface is mobile. Its upper part becomes extended as the bubble floats upwards while the lower part is compressed[3,4]. The new surface regions produced are filled with the adsorbable substance, while the contraction of the surface results in its desorption. On the upper half of the rising bubble, the degree of adsorption is lower than on a stationary surface (Γ_0), which ensures a continuous supply of the surfactant (or of adsorbable inorganic ions) from the bulk phase to the expanded surface. On the lower half of the rising bubble, the degree of adsorption is higher than Γ_0, which gives rise to the desorption of the surfactant. Thus the degree of adsorption $\Gamma(\theta)$ increases in the direction of the migration of the surface of the bubble, i.e. from the upper pole ($\theta = 0$) to the lower pole ($\theta = \pi$).

The supply of the surfactant to the upper half of the bubble and the removal to the bulk phase of the surfactant desorbed from the lower half take place owing to the existence near the surface of the so-called diffusion boundary layer. Its thickness is much smaller than the radius of the bubble R and is defined by the formula

$$\delta = R/\mathrm{Pe}^{1/3} \quad , \qquad (24)$$

where Pe is the Peclet number defined by the expression

$$\mathrm{Pe} = \frac{RU}{D} = \mathrm{Re}\,\frac{\nu}{D} \quad . \qquad (25)$$

Since the diffusion coefficient $D \cong 10^{-5}$ cm^2 s^{-1} and $\nu/D \cong 10^3$, in the relevant range of Reynolds numbers the quantity Pe should be large (~10^4–10^6); the surfactant concentration in the diffusion boundary layer on the upper half of the bubble is smaller than in the bulk phase and increases from the upper to the lower pole, as in the dynamic adsorption layer. For any specified angle θ, which is reckoned from the upper pole, equilibrium between the degrees of adsorption $\Gamma(\theta)$ and the volume concentration in the bulk of the diffusion layer directly at the surface $c(R, \theta)$ persists:

$$\frac{\Gamma(\theta)}{c(R, \theta)} = \frac{\Gamma_0}{c_0} \qquad (26)$$

where Γ_0 is the equilibrium degree of adsorption on the surface of a stationary bubble at a surfactant concentration in the bulk of the solution c_0.

Not only the movement of the bubble surface influences the formation of a dynamic adsorption layer; the opposite influence of the dynamic adsorption layer on the movement of the surface also obtains. The degree of adsorption increases in the direction of motion of the liquid, while the surface tension σ falls. This leads to the generation of forces directed in opposition to the stream of liquid and retarding the movement of the surface. Thus the theory of the dynamic layer must be based on the simultaneous

†During the preparation of this article for the press, we learnt of the communication by Anfruns and Kitchener[98], in which they described an experimental confirmation of the above considerations.

solution of the equation for diffusion, complicated by allowance for the influence of the movement of the surface on adsorption–desorption processes, and the hydrodynamic equations complicated by the influence of the adsorption layer on the movement of the interface between the liquid phases[68–71].

The simultaneous allowance for the influence of the hydrodynamic field on the distribution of adsorption and volume concentration and for the influence of dynamic adsorption on the velocity field for Pe $\gg$ 1 has been achieved in the limiting cases of weak (Re $\gg$ 1) and strong retardation of the surface (Re $\ll$ 1).

For weak retardation of the main section of the surface and for a moderate surface activity, i.e. when

$$\Gamma_0/c_0 \ll \delta \quad , \tag{27}$$

the change in the degree of adsorption is slight: $\Gamma_0 - \Gamma|_{\theta=0} \ll \Gamma_0$. The angular relation $\Gamma(\theta)$, obtained by Deryagin et al.[3], can be roughly approximated by a cosine, as assumed by Frumkin[69], only on the upper half of the bubble. A virtually uniform and weak retardation of the surface can be characterised by the retardation coefficient

$$\gamma = \frac{2}{3}\frac{\partial\sigma}{\partial c}\Gamma_0 \mathrm{Pe}^{-1/3} D^{-1} \tag{28}$$

and $\gamma \ll \eta$.

For weak retardation and a high surface activity, i.e. when

$$\Gamma_0/c_0 \gg \delta \quad , \tag{29}$$

the degree of adsorption on the main section of the bubble surface is much smaller than the equilibrium value and a very rapid growth of adsorption and a strong inhibition of the surface should be observed only for $\theta \to \pi$.[4]

In connection with the influence of the surface on the adsorption layer discussed above, the problem arises of the change in the structure of the electrical double layer along the mobile bubble surface. A characteristic feature of the structure of the equilibrium double layer at the air–water interface is that it is caused by the negative and not positive adsorption of ions. Numerous experimental studies, which have been reviewed[73,74], have established that the surface tension in solutions of inorganic electrolytes increases. According to the Gibbs formula, this indicates negative adsorption. The magnitude of the effect is frequently characterised by the thickness of the ion-free layer (h). This thickness is of the order of magnitude of the size of water molecules. The expulsion of ions from the surface layer is caused by their electrostatic interaction with the interface, which can be characterised in terms of electrostatic image forces.

In order to test the validity of condition (27), one can use the following estimate:

$$(\Gamma_0/c_0) \simeq h \simeq 10^{-7}\ \mathrm{cm} \ll \delta \quad . \tag{30}$$

Thus condition (27) is valid, which means that, under the conditions of negative adsorption, the double layer is hardly deformed on the mobile bubble surface.

On passing from the Stokes field of the bubble to the potential field, the stripping hydrodynamic force increases by a factor R/a, since the radial flow rate of the liquid at the distance of closest approach of the centre of the particle to the surface of the bubble (a) increases by the same factor. This difference between the Stokes and potential regimes in the treatment of the possibility of the breaking away of particles diminishes somewhat if account is taken of the retardation of the bubble surface. On the fully retarded section of the bubble surface, the radial component of the velocity of the liquid at a distance y from the surface of the bubble diminishes according to a quadratic law for $y \ll R$, as in the Stokes regime. On a partly retarded section of the surface, the charge proceeds in accordance with a linear law but with a coefficient which is comparable to the ratio of the local retardation coefficient to the viscosity of water. The higher the degree of retardation of the bubble surface, the smaller the possibility that the particles will break away in contact-free flotation. For this reason, the question of the degree of retardation of the surface is of great interest.

The literature data[54,75] presented in Fig.7 show that, for Re > 40, the velocity of the bubble is greater the lower the concentration of the surfactant introduced and that, for Re < 40, bubbles rise as solid spheres even when the water has been very carefully freed from impurities. The agreement of the rate at which the bubble rises with the value calculated for a solid sphere is regarded by many investigators as the criterion of the retardation of the entire surface of the bubble. In the light of theoretical studies of the retardation of the movement of the bubble surface, this condition is believed to be necessary but not sufficient. When a considerable proportion of the bubble surface is retarded, some of it, near the upper pole, can retain mobility[70]. There is also a possibility of a uniform, strong, but incomplete retardation of the entire surface[71,72]. In both cases the rate at which the bubble rises can be the same, within the limits of the error of the measurement, as that for a solid sphere. However, the degree of adsorption of the surfactant at the upper pole can then be much less than Γ_0.[71,72]

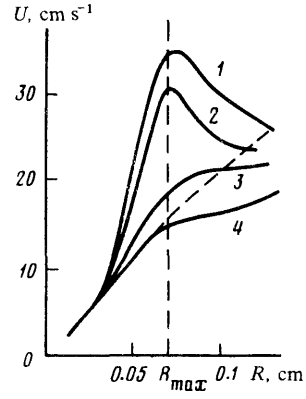


Figure 7. The rate of the rise of bubbles in aqueous solutions of sodium dodecyl sulphate: *1*) distilled water; *2*) 10^{-6} M; *3*) 1.2×10^{-5} M; *4*) 10^{-3}–10^{-4} M. The dashed curve corresponds to bubbles with a fully retarded surface in distilled water or a millimolar solution[54].

The hydrodynamic resistance, which determines the rate of the upward rise of the bubble, consists of the shape resistance, which depends on the position of the line at which the particle breaks away, and the viscous resistance, which depends on the degree of retardation of the entire surface. Since the contribution of the viscous resistance is not small, one must assume that, for Re < 40, the entire lower half of the bubble is retarded, since otherwise the velocity of the bubble would have differed significantly from

the velocity of the solid sphere owing to the contribution of the viscous resistance. Hence follows the important conclusion that, at Re < 40, the stripping force increases insignificantly compared with the Stokes regime.

The transitional regime (1 < Re < 40) can be optimal for reagent-free flotation. Its advantage over the Stokes regime consists in the fact that, when it obtains, the possibility of fixation at the primary energy minimum increases. A necessary condition for reagent-free flotation is sufficient depth of the primary energy minimum. If this condition does not hold, then ionogenic surfactants must be introduced to prevent the breaking away of the particles.

The agreement of experimental data for the rates at which bubbles rise with the calculated values[54], obtained on the assumption that the surface is unretarded implies that, at Re > 40, a considerable proportion of the lower half of the bubble is mobile, to which corresponds a sharp increase of the normal component of the velocity responsible for the breaking away of the particles. Therefore, on passing to the condition where Re > 40, contact-free flotation becomes hindered. Hence the introduction of an ionogenic surfactant is necessary even when the adhesional hydrodynamic force ensures the overcoming of the disjoining pressure, except in the case where the depth of the primary well is large or contact flotation obtains.

The introduction of a cationic surfactant (for a negative particle charge) leads to three effects ensuring flotation, namely the difficulty associated with the overcoming of the disjoining pressure in the deposition of particles on the bubble is eliminated, attraction forces (stronger under certain conditions than the van der Waals forces) preventing the breaking away of the particles are ensured and, as a result of the retardation of the movement of the lower half of the bubble surface, the stripping hydrodynamic force diminishes.

The consumption of the ionogenic surfactant should ensure the neutralisation of the bubble charge, which can be roughly estimated by specifying the surface potential ψ, as was done by Ekserova and Zakharieva[76]. It follows from the Gouy–Chapman theory that

$$\sigma = F\Gamma' = Fc_e\varkappa^{-1}\sinh(\Psi/2) \qquad (31)$$

where Γ' is the degree of adsorption of the cationic surfactant necessary for the neutralisation of the bubble charge at an electrolyte concentration c_e and $\varkappa^{-1}$ is the thickness of the diffuse component of the double layer. The consumption of the surfactant should ensure a fairly high degree of adsorption, i.e. the following relation should hold:

$$\Gamma > \Gamma' \simeq c_e\varkappa^{-1}. \qquad (32)$$

In the most important case where

$$\varkappa^{-1} \ll \delta \qquad (33)$$

conditon (32) can be ensured both for low and high surface activities. The use of surfactants with a very high surface activity, corresponding to condition (29), is undesirable since the adsorption layer is then displaced to the lower pole of the bubble. The introduction of such a surfactant does not facilitate the deposition of particles on the upper half of the bubble and does not prevent their breaking away from the lower half, since the surfactant is concentrated in the small region near the lower pole of the bubble and the particles can break away from any section of the surface near which the normal component of the velocity is directed into the bulk of the liquid. By increasing the concentration c_0, it is possible to expand the retarded zone. This question has been considered by Dukhin and Buikov[71,72], but these investigations do not answer the question whether the retardation of the entire lower half of the bubble is possible at a sufficiently high c_0.

The use of surfactants with a very low surface activity is inconvenient, since it is associated with an excess consumption of the reagent. The same necessary degree of adsorption Γ' can be ensured at a lower concentration c_0 the higher the ratio Γ_0/c_0 within the limits of the validity of condition (27). With increase of Γ_0/c_0, the retardation coefficient also increases [see Eqn.(28)] even for an equivalent decrease of c_0, which is also important for the prevention of the breaking away of the particle. One may therefore conclude that it is useful to employ surfactants with a surface activity such that $\Gamma_0/c_0 \cong \delta$. A surfactant concentration equal to

$$c_0 = \frac{c_e\varkappa^{-1}}{\delta} \qquad (34)$$

is then necessary to ensure condition (32). At this retardation concentration γ may be comparable to the viscosity, which shows that a certain section of the bubble surface is retarded, because the following relation holds:

$$\frac{\gamma}{\eta} = \frac{2}{3}\frac{\partial\sigma}{\partial c}\Gamma_0 \mathrm{Pe}^{-1/4}D^{-1}\eta^{-1} \simeq \frac{RT}{\eta U}\varkappa^{-1}c_e \ . \qquad (35)$$

VII. NON-EQUILIBRIUM SURFACE FORCES IN FLOTATION

A characteristic feature of the mechanism of the deformation of the thin double layer by various kinds of external influences is that equilibrium conditions, particularly the electroneutrality condition, hold for each section of the surface[3,77]. The degrees of adsorption (surface charge) and the concentration in the diffusion layer vary along the mobile surface of the bubble. Thus the thickness of the double layer varies along the surface of the bubble in accordance with the variation of the surface charge and the electrolyte concentration but on each section of the surface its three-dimensional double layer structure is described by the equilibrium theory. This justifies the consideration of the elementary step in flotation on the basis of the theory of heterocoagulation. However, qualitatively new effects also arise on formation of the double layer. Diffusion in an electrolyte is known to be usually coupled with the generation of an electric field. The vector lines of the electric field E_D coincide with the vector lines of the concentration gradient grad c. In a binary electrolyte solution the electric field strength is expressed in terms of the local concentration gradient by the familiar formula[3,78]

$$E_D = \frac{D^+ - D^-}{z^+D^+ + z^-D^-}\frac{RT}{F}\frac{\mathrm{grad}\,c}{c} \ , \qquad (36)$$

where D^+, D^-, z^+, and z^- are the diffusion coefficients and the electrovalences of the anions and cations and F is the Faraday. An electric field should therefore arise within the limits of the diffusion boundary layer coupled with the dynamic adsorption layer of the ionogenic surfactant. This is caused by the slight deviation from the electroneutrality condition. Like the grad c vector lines, the E_D vector lines begin at the upper boundary of the quasi-equilibrium double layer, are oriented approximately at right angles to the surface, and terminate at a point within the diffusion layer. However, the sources of electric field lines are known to be positive charges, while negative charges diminish the field. Hence it follows that charges of opposite sign, approximately cancelling out, are localised within the limits of the quasi-equilibrium double layer and

in the diffusion layer (Fig.8). These two layers of charges constitute a single system in the sense that the change in the distribution of charges of one layer is necessarily accompanied by redistribution of charges in the other layer.

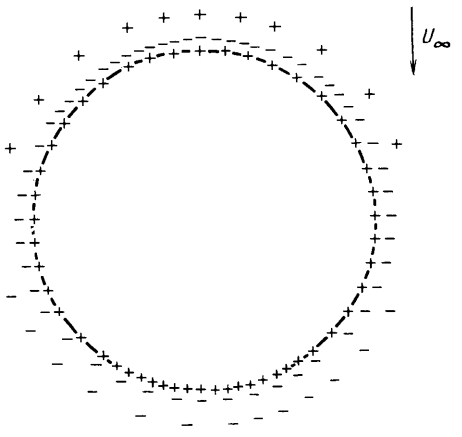


Figure 8. Distribution of the charge signs in the primary and secondary double layers for a substance with moderate surface activity[5].

This system of charges, arising on deformation of the equilibrium double layer, can be naturally called the secondary double layer[78-80]. Since the thickness of the secondary double layer exceeds that of the equilibrium double layer by several orders of magnitude (except at low electrolyte concentrations), the deposition of particles on the surface of the bubble can be controlled under certain conditions primarily by the stage in which the particles pass through the diffusion layer[81]. The consideration of this question simplifies if the particle size is less than δ, so that a particle passing through the diffusion layer can be regarded as subject to homogeneous electric and diffusion fields. Consequently a particle crossing the diffusion layer is subjected to electrophoresis and diffusiophoresis[82,83].

In a study of the deposition under gravitational forces of galenite particles of different size on the mobile surface of a fixed bubble from a vertical stream of liquid[9], it was observed that particles whose size is below a critical value a_{cr} do not reach the surface of the bubble. On the basis of the measured values of ζ, it was established that, for $a < a_{cr}$, the joint action of electrophoresis and diffusiophoresis is responsible for the force repelling the particles from the bubble, which exceeds the gravitational force. With increasing electrolyte concentration, the repulsion force weakens, which is revealed experimentally by a decrease of a_{cr}.

The thickness of the diffusion layer of a freely rising bubble is much smaller, in view of its high velocity, than in the experiments described. The effect can therefore appear only for particles which are so small that their thermal motion is significant. Electrophoresis and diffusiophoresis must be taken into account in the description of the Brownian diffusion of submicron particles to the mobile surface of a bubble and at a fairly low electrolyte concentration. It has been shown[84] that the concentration drop in the diffusion layer δc is very small when the surface of the bubble is fully mobile:

$$\frac{\delta c}{c} \simeq \frac{\mathrm{Pe}^{1/3}}{(\varkappa a)^2} \quad . \tag{37}$$

The mechanism of the action of non-equilibrium surface forces for particles whose size exceeds δc can be established fairly simply only when the same ionogenic surfactant is sorbed on the surfaces of the bubble and the particle. This mechanism is associated with the desorption of the reagent from the surface of the particle, diffusion through the film, and adsorption on the surface of the bubble. The diffusional transport of the adsorbate is caused by the decrease of the concentration of the reagent in the diffusion layer of the bubble, which extends over the upper half of the bubble and, when condition (29) holds, also over a considerable proportion of the lower half. The section of the bubble surface where adsorption takes place acquires an excess charge, whose sign is the same as that of the rapidly diffusing ion. An equal charge of the opposite sign arises on the section of the surface of the particle from which the reagent is desorbed. An estimate showed that an electric field of $\sim 10^3$ V cm arises under these conditions. The excess charges of the bubble are attracted to the excess charges of the particle, so that the interfacial film is as it were clamped between the plates of a condenser, as a result of which its thickness diminishes. The non-equilibrium surface forces decrease in the presence of an indifferent electrolyte if its concentration is much greater than that of the ions in the adsorption layer. For a quantitative estimate of this important factor, which reduces the non-equilibrium surface forces, it is necessary to extend the theory[8] developed in relation to a binary electrolyte to the case of three kinds of ions.

High electrolyte concentrations have only a weak influence on the non-equilibrium surface forces due to the dynamic adsorption layer of the non-ionogenic surfactant[85,86]. In the course of migration along the mobile surface of the bubble the surfactant concentration in the diffusion boundary layer in the vicinity of the particle increases continuously. Therefore in the centre of the interfacial film the concentration of the surfactant and the degree of adsorption are lower than on the periphery of the film, where the concentration increases continuously as a result of the migration of the particle along the diffusion layer. Since the degree of adsorption at the centre of the interfacial film is smaller than on its periphery, the surface tension at the centre of the film is higher. The increase of the surface tension towards the centre of the film from its periphery should be accompanied by surface flow from the periphery to the centre, involving the entire liquid of the film. The flow of liquid into the gap between the particle and the bubble prevents a decrease of the thickness of the film and rules out the possibility of flotation. This analogue of the Marangoni–Gibbs effect does not arise if the surface of the bubble is stationary and the degree of adsorption does not change along it.

The decrease of the collision efficiency due to this effect has been calculated[99] for spherical and disc-shaped particles under the conditions of a weak retardation of the surface and a moderate adsorbability of the surfactant, satisfying condition (27). For a disc-shaped particle, the collision efficiency can diminish by several orders of magnitude. For spherical particles, the diffusional exchange in the interfacial film between the centre of the latter and its periphery is more intense, which leads to a decrease of the drop in adsorption and surface tension, i.e. a weakening of the effect. However, the deposition of even a spherical

particle is possible only in the small region near the upper pole of the bubble.

The effect involving the stabilisation of the interfacial film discussed above can weaken if the surfactant is adsorbed not only by the bubble but also by the particle. There is then a possibility of the diffusional transfer of the surfactant from the surface of the particle to the surface of the bubble, which should lower the surface tension at the centre of the interfacial film, compensating to some extent its increase as a result of the tangentian movement of the particle.

Diffusional non-equilibrium surface forces have been observed experimentally[87,88]. A thin layer of soluble ionogenic surfactant was first deposited on a small section of an inclined surface of the solid. When water had flowed off the surface, the thickness of the inclined surface layer under stationary conditions was always constant except for the section coated by the surfactant. Over the surfactant-coated section, the film became appreciably thinner under the influence of the surfactant. Since the surface of the film in the attenuated region was significantly curved, the authors[87,88] reached the completely correct conclusion that appreciable forces, which must compensate for the capillary pressure due to the curvature of the surface of the film, act at right-angles to the water–air interface. A theory of this effect has been proposed[89], taking into account the electro-capillary effects, which were significant in both the experiments of Evans and Ewers[87,88] and in the application of ionogenic surfactants in the flotation of small particles.

By introducing ionogenic surfactants, it is possible to eliminate the hindrance of the flotation of small particles associated with the operation of equilibrium surface forces (neutralisation of the charge of the bubble and decrease of the electrostatic component of the disjoining pressure), but the effect of the stabilisation of the interfacial film can then be considerable, as a result of which flotation is impaired. The introduction of ionogenic surfactants in flotation by small bubbles therefore appears to be more reliable, since in the Stokes regime one may expect the complete retardation of the surface of the bubble and a sharp weakening of the non-equilibrium surface forces. This can also be achieved in the transitional regime by increasing the consumption of the reagent, ensuring thereby the retardation of the surface.

VIII. THE EFFICIENCY OF THE COLLISION AND FLOTATION KINETICS

Flotation is usually carried out with large volume fractions of bubbles, which leads to an appreciable deviation of the distribution of the velocities of the liquid in the vicinity of the bubbles compared with the case of a single bubble discussed above. As a result of allowance for the velocity distribution engendered by the system of bubbles[17], a formula was obtained for the capture efficiency. The efficiency depends not only on the bubble size but also on the fraction of dispersed gas[18]. The study of the flotation of monodisperse particles by a system of bubbles led to the formula

$$n(t)=n_0e^{-kt} \quad , \tag{38}$$

which had been obtained earlier in another study[90]. Here $n(t)$ and n_0 is the concentration of particles at time t and the initial concentration. Under these conditions, the following expression was obtained for k (in the case of monodisperse systems):

$$k=\frac{3qE}{4R} \tag{39}$$

where q is the rate of bubbling, equal to the volume of gas blown across a unit cross-sectional area of the flotation chamber per unit time. This formula was extended[17] to the case of polydisperse systems and it was found that under conditions of a nearly normal distribution of particles to the bubbles, one may use Eqn.(39) in which the statistical mean particle and bubble sizes are employed.

Thus the kinetic theory of the flotation of small particles described above makes it possible to relate the technologically most important parameter k to the measured characteristics of the flotation system. The parameter k can be related to E also when particles with sizes greater than a_{max} can break away after deposition. In the summation with respect to fractions of deposited particles [in the integration of $E(a)$] it is sufficient to use a_{max} as the upper integration limit.

IX. THE INFLUENCE OF THE AGGREGATION OF PARTICLES ON THE ELEMENTARY STEP IN NON-INERTIAL FLOTATION

The introduction of surfactants in order to reduce the electrokinetic potential [of the bubble?] can lead simultaneously to a decrease of the electrokinetic potential of the particles and hence to their aggregation. The influence of aggregation on the elementary step in flotation has been considered[20] on the assumption that the aggregate is rigid and spherical in shape and that its radius a^* is small compared with R. With these simplifying assumptions, the efficiency of the collision of the aggregate with the bubble E^* can be described by Eqns.(13) and (14) having replaced the particle radius a by the radius of the aggregate a^*. Then the following estimates can be obtained from Eqns.(13) and (14) for the intensity of the deposition of particles on the bubble as a result of aggregation in relation to the Stokes and potential regimes:

$$E_s^*/E_s \simeq (A/a)^2;\ (E_p^*/E_p) \simeq a^*/a \ . \tag{40}$$

Since under the conditions of the short-range hydrodynamic interaction, there is a possibility of the outflow of the liquid from the film separating the bubble and the aggregate into the pores within the aggregate, the attenuation of the film is faster and the ratio E^*/E may prove to be greater than that found by Eqns.(40).

The increase in the size of the aggregate plays a positive role in flotation only at the stage involving the formation of the aggregate–bubble system, since the probability that the aggregate will break away from the bubble increases simultaneously. Indeed, the greater the size of the aggregate or particle, the greater the radial component of the velocity at the centre of the aggregate, which is oriented outwards at right angles on the lower half of the surface of the bubble. Formulae have been obtained[20] for the stripping hydrodynamic force and the maximum radius of the bubble capable of flotation without the breaking away of aggregates of given radius. The derivation of the formulae was based on the solution[91,92] of the hydrodynamic problem of two spheres rising upwards along a common axis in the Stokes regime.

For a given bubble size, there is an optimum size of the aggregate ensuring the most intense flotation, since larger aggregates break away from the surface of the bubble and smaller aggregates are deposited on its surface at a lower frequency. It is inconvenient to increase appreciably the size of the bubble, since, under the conditions of a simultaneous decrease of the size of the aggregate, this leads to a sharp diminution of the ratio of the volumes of the aggregates undergoing flotation and of the gas bubbled

through the system. An appreciable decrease in the size of the bubble is also inconvenient, because the rate of transport of the aggregates by the bubbles decreases sharply at the same time. This means that there is an optimum bubble size for the flotation of aggregates of given dimensions. Unfortunately, it is difficult to estimate this optimum reliably. Firstly, it is difficult to estimate the number of aggregate particles in contact with the bubble, in proportion to which the force acting against the stripping force increases. This number depends on the deformation of the aggregate under the influence of the adhesional hydrodynamic force and the tangential stream of liquid. Secondly, the aggregate may break away owing to the rupture of the coagulation linkage between the particle adhering to the bubble and the neighbouring particles of the aggregate.

X. THE FLOTATION OF SUBMICRON PARTICLES

With decrease of the radius of the non-inertial particles and when the latter attain the region of submicron dimensions, they acquire the capacity for intense Brownian diffusion. In this case the electrostatic barrier impenetrable to comparatively large but non-inertial particles can be overcome by small "Brownian" particles owing to the energy of their thermal movement.

The efficiency of the capture of Brownian particles by the bubble can be determined by solving the equation for the convective diffusion of particles to a spherical obstacle in the field of the forces of interaction between the particles and the bubble. It is then possible to isolate two limiting cases. If the interaction force promotes rapid adhesion of the particles to the surface of the bubble, then the rate of deposition and hence the capture efficiency will be limited by the rate of diffusion of the particles to the surface of the bubble. It follows from the work of Ruckenstein and Prieve[93] and Spielman and Friedlander[94] that the efficiency of the capture of particles by a bubble rising under the conditions of small Reynolds numbers and having a fully retarded surface is then expressed by the formula

$$E_s = \frac{3}{2\Gamma(4/3)}\left(\frac{D_a^2\pi^2}{3R_s^2U_s^2}\right)^{1/3}, \qquad (41)$$

where Γ is the gamma-function and D_a the diffusion coefficient of the particles. On the other hand, if the bubble rises in the potential regime ($Re \gg 1$) and its surface is fully mobile then, as shown by Rulev[95], the capture efficiency is defined by the expression

$$E_p = \left(\frac{32D_a}{\pi U_p R_p}\right)^{1/2}. \qquad (42)$$

If the deposition of the particles on the surface of the bubble is hindered by their interaction (for example, electrostatic), then the capture efficiency will be limited solely by the rate of diffusion in the field of surface forces. In this case

$$E = \frac{4K}{U}, \qquad (43)$$

where K is the deposition rate constant which is determined by the energy of the interaction of the particle with the bubble. If we denote this energy by ϕ, then it follows from the work of Ruckenstein and Prieve[93] that the following expression is valid:

$$K = \frac{1}{D}\int_0^\infty \left\{\exp\frac{[\varphi(h)/kT]}{f(h/a)} - 1\right\} dh, \qquad (44)$$

$$f(H) = \begin{cases} \dfrac{H}{1+H} \text{ when } H = \dfrac{h}{a} \leqslant 1 \\ \dfrac{H - 1/8}{H+1} \text{ when } H \to \infty . \end{cases} \qquad (45)$$

Eqns.(41) and (42) show that, in contrast to the second case, in the first case the capture efficiency is determined exclusively by the diffusion coefficient, which is inversely proportional to the particle radius. Hence it follows that

$$E_s \propto a^{-2/3}, \; E_p \propto a^{-1/2}, \qquad (46)$$

i.e. the capture efficiency increases with decreasing particle radius in the submicron region, which has in fact been observed experimentally[55].

Thus, with decrease of the particle radius and on transition from the non-inertial deposition regime to the diffusional regime, a minimum in capture efficiency is observed in the region of $a \cong 0.1$ μm. The intensification of the flotation of particles of this size is particularly important and can be achieved by means of their aggregation.

If one excludes from consideration effects complicating the elementary step in flotation at a fairly low electrolyte concentration and for a fairly large bubble size, then the theory developed here, whose fundamental postulates have already been confirmed experimentally, indicates ways of optimising the purification of water by flotation. In the absence of non-electrostatic stability factors and at an electrolyte concentration above the threshold value, one must test the possibility of reagent-free flotation. On the other hand, if the level of the electrolyte concentration in the water to be purified is low or when a non-electrostatic stability factor is characteristic of the particles, then their fixation on the surface of the bubble must be ensured by introducing ionogenic surfactants.

The intensity of extraction in water purification by flotation and the possibility of increasing the productivity of flotation water purification plants without increasing their size can be achieved by employing bubbles of optimum dimensions and at the optimum concentration. In this connection one should note that the experience gained in water purification by flotation, although the latter has so far been developing solely on an empirical basis, is consistent with the hydrodynamic theory described. Indeed, in order to ensure an acceptable rate of extraction of disperse contaminations by flotation, one resorts to small bubbles, which corresponds to an increase in the efficiency of particle capture by the bubble as its size diminishes. Instead of flotation by large bubbles, formed on mechanical dispersion of air, in water purification one employs electroflotation, microflotation, flotation by bubbles evolved from supersaturated solutions of air in water, i.e. methods ensuring bubbles of small size. The observed intensification of flotation on passing to small bubbles (electroflotation, microflotation) can be associated with the weakening of the forces tending to strip the particles off the bubble. However, for maximum rates of extraction of disperse contaminations, one must use bubbles which are not simply small but have the optimum size.

Full control of the flotation of small particles can be achieved only by studying the entire set of problems associated with the hydrodynamics and stability of thin films which are and are not in equilibrium with surface forces.

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Kinetics and Mechanism of the Oxidation of Aliphatic Amines

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Data on the kinetics and mechanism of the oxidation of aliphatic amines by various oxidants are surveyed and examined critically.
The bibliography includes 205 references

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I. INTRODUCTION

Only that part of the extensive literature on the oxidation of aliphatic amines in which problems of the kinetics and mechanism of the oxidation reaction are considered is surveyed. These studies are of considerable and general interest to organic chemists as an example of the current approach to the problem of the mechanisms of complex reactions. They are of interest also to biochemists in view of the biological importance of aliphatic amines.

Our aim was to find common features in the oxidative reactions of aliphatic amines, to understand the causes of the differences between them, to examine the existing ideas about the mechanism, and to give a critical and general compilation of the entire set of the available data. We do not include studies on photochemical oxidation, electrochemical oxidation, and the interaction of amines with free radicals, since modern reviews of the literature on these problems are available[1-3].

II. INTERMEDIATE OXIDATION PRODUCTS

Non-aromatic ammonium radical-cations $RR'R''\dot{\overset{+}{N}}$ are formed in various reactions of amines, their derivatives, and certain other nitrogen-containing compounds. Their structure and properties have been thoroughly investigated (see the latest review on this problem[4]).

The simplest ammonium radical-cations have a planar structure. They are extremely unstable, but their stability can be made appreciable or increased for radical-cations corresponding to triethylenediamine or olefins with $N(CH_3)_2$ groups at the double bond. In weakly acid, neutral, or basic media the above species rapidly lose a proton at the α-carbon atom and give rise to α-amino-radicals;

$$\dot{\overset{+}{R}}CH_2\ddot{N}R'_2 \xrightarrow[-H^+]{} \dot{\overset{-}{R}}CH-\ddot{\overset{+}{N}}R'_2 \longleftrightarrow \dot{\overset{-}{R}}CH-\ddot{N}R'_2 \quad . \qquad (1)$$

This reaction is usually much faster than the abstraction of an $H^\cdot$ atom from the medium by the radical-cation; it is retarded in a strongly acid medium. Species of the type $RR'\dot{\overset{+}{N}}H$ are stronger acids by several orders of magnitude than $RR'\dot{\overset{+}{N}}H_2$.

The existence of α-amino-radicals has been demonstrated and their EPR spectra have been studied[5]. Their chemical properties have not been investigated by direct methods; all the available information about them is hypothetical and is based on indirect data obtained by studying the oxidation of amines in the intermediate stages of which the formation of α-amino-radicals is postulated. In the oxidation of amines α-amino-radicals can be obtained not only via reaction (1) but also as a result of the abstraction of $H^\cdot$ from the α-carbon atom in amines. Under oxidation conditions, the radicals undergo further rapid reactions, probably via two pathways—with electron transfer to the oxidant and the formation of immonium ions:

$$RCH_2\dot{C}H-\ddot{N}R'_2 + Ox \xrightarrow[-Ox^-]{} RCH_2\overset{+}{C}H-\ddot{N}R'_2 \longleftrightarrow RCH_2CH=\dot{\overset{+}{N}}R'_2$$

or by transition with the oxidation of a hydrogen atom and the formation of an enamine:

$$RCH_2\dot{C}H-\ddot{N}R'_2 + Ox \xrightarrow[-OxH]{} RCH=CH-\ddot{N}R'_2 \quad .$$

Enamines can be obtained also from immonium ions:

$$RCH_2\overset{+}{C}H-\ddot{N}R'_2 \longleftrightarrow RCH_2CH=\dot{\overset{+}{N}}R'_2 \xrightarrow[-H^+]{} RCH=CH-\ddot{N}R'_2 \quad .$$

Radicals of the type $R\dot{C}H-NHR'$ are also capable of disproportionating:

$$2R\dot{C}H-NHR' \rightarrow RCH=NR' + RCH_2NHR' \quad .$$

The radicals of the last type as well as $RCH_2\dot{N}H$ can give rise to imines also by losing $H^\cdot$ atoms as a result of oxidation.

Among the properties of the immonium ions $RR'C=\dot{\overset{+}{N}}R''_2$ and imines $RR'C=NR''$, we may mention their tendency to hydrolyse with formation of aldehydes or ketones and dealkylated initial amines. This tendency depends on the structure and the reaction conditions. Sometimes the hydrolysis is slow or does not occur at all and the imines are the main oxidation products. We may also mention the capacity of certain imines for polymerisation, which can lead to tarry products.

Carbinolamines $R_2NCH(OH)CH_2R'$ are formed when secondary amines interact with aldehydes. They are unstable and, as regards their properties, we shall mention their ability to hydrolyse in an acid medium with formation of the initial amine and an aldehyde and to undergo dehydration to the enamines $R_2NCH=CHR'$ (see, for example, Henbest and Stratford[6]).

A significant feature of the properties of enamines (vinylamines)[7] is that these compounds readily hydrolyse in an acid medium to carbonyl compounds and dealkylated initial amines and that enamines containing hydrogen at the nitrogen atom are in tautomeric equilibrium with imines:

$$RR'C=CR''-NHR''' \rightleftharpoons RR'CH-CR''=NR'''.$$

III. THE OXIDATION REACTIONS OF ALIPHATIC AMINES

1. Oxidation by Iodonium Salts

The interaction of iodonium salts $Ar_2I^+X^-$ with amines has been widely investigated[8-12] under various conditions. These reactions give rise to the salts of the initial amines, the

products of the reduction of the iodonium salts (iodoarenes), and the compounds ArH and Ar—Ar. In certain cases a nitrogen-containing resin is also obtained.

This composition of the products serves as an argument in support of a radical reaction mechanism. The latter has been confirmed by the formation of diphenylmercury in the interaction of $(C_6H_5)_2I^+BF_4^-$ with diethyl- or triethyl-amine in the presence of mercury[8,9]; the following reaction mechanism has been proposed:

$$Ar_2I^+X^- + NR_3 \rightleftharpoons [Ar_2I : NR_3]^+ X^- \rightarrow Ar_2\dot{I} + \overset{+}{N}R_3X^-$$
$$Ar_2\dot{I} \xrightarrow{-ArI} \dot{A}r \xrightarrow{+\dot{A}r} Ar-Ar$$
$$\overset{+}{N}R_3X^- + \dot{H} \rightarrow \overset{+}{N}HR_3X^- \ .$$

By analogy with aromatic amines[13] and spectroscopic data[9], it has been suggested that the first stage involves the formation of a donor—acceptor complex, whose homolytic decomposition leads to the products.

This mechanism does not reflect the entire complexity of the reactions of amines with iodonium salts (see below). We may also mention that its last stage requires revision, since ammonium radical-cations rapidly split off protons, particularly in basic media. One can therefore postulate that ammonium salts are formed via the reactions

$$R_2\overset{+}{N}HX^- + R_2NH \rightarrow R_2\dot{N} + R_2\overset{+}{N}H_2X^- \text{ (for primary and secondary amines);} \quad (2a)$$
$$R_3\overset{+}{N}CH_2R'X^- + R_3N \rightarrow R_2N\dot{C}HR' + R_3\overset{+}{N}HX^- \text{ (for tertiary amines).} \quad (2b)$$

Apparently the main pathway, leading to the formation of biaryls, consists in the addition of radicals Ar$^\cdot$ to the compounds ArH and the splitting off of H$^\cdot$ from the resulting cyclohexadienes.

An alternative reaction mechanism, possible only in an aqueous medium, namely homolytic decomposition of diaryliodonium hydroxide, has been rejected[11] on the grounds that the decomposition of $Ar_2I^+OH^-$ is slower than the interaction of iodonium salts with amines and gives rise to other products.

The formation of arylated amines (which are the main products according to some data, for example, those of Beringer et al.[14]) in the reactions considered has also been explained by a radical mechanism[10]):

$$Ar_2\dot{I} + \ddot{N}H_2R \xrightarrow{-ArI} ArNHR + \dot{H}$$

However, one cannot rule out the possibility that nucleophilic substitution of iodonium salts by amines takes place simultaneously with the homolytic reaction[14] and that the arylated amines are formed via this mechanism. We may note that the simultaneous occurrence of nucleophilic and radical reactions has been established in the interaction of iodonium salts with alkoxides[15].

An unambiguous proof of the involvement of radicals in the reactions of amines with iodonium salts has been obtained with the aid of chemically induced nuclear polarisation (CIDNP) and EPR. Chemically induced nuclear polarisation arises in radical pairs and is manifested by anomalies in the NMR spectra of the reaction products of the radicals in these pairs. The reaction kinetics can be inferred from the CIDNP kinetics[16]. In the case considered CIDNP was observed in the benzene obtained by the interaction of iodonium salts with *N,N'*-tetramethyl-*p*-phenylenediamine (TMPA) or triethylamine. At the same time the TMPA radical-cations were detected[17,18]. These data have been treated[17,18] as evidence proving electron transfer from the amine to the iodonium salt in the key stage of the reaction. However, kinetic studies have shown that the mechanism is much more complex.

The kinetics of the oxidation of amines by diphenyliodonium chloride have been investigated in several studies. Reactions with di-n-butylamine[19], ethanolamine[20], and triethylamine[21] proved to have a radical-chain mechanism. They have an inductive period the duration of which is increased by the addition of inhibitors of radical-chain processes. CIDNP in the resulting benzene and iodobenzene is observed under certain conditions. The kinetic equations for the reactions with ethanolamine and triethylamine have the same form (here Am = amine):

$$w = k[Ph_2I^+Cl^-][Am] \ . \quad (3)$$

However, this form changes for dibutylamine, for which the following equation is valid in the presence of an excess of the amine:

$$w = k[Ph_2I^+Cl^-]^2, \ w_0 = k_0[Ph_2I^+X^-] \ , \quad (4)$$

where w_0 and k_0 are the rate of initiation and the initiation rate constant†.

The following mechanism of the reaction with triethylamine corresponds to Eqn.(3).

$$(C_6H_5)_2I^+ + (C_2H_5)_3N \xrightarrow[S]{\text{fast}} [(C_6H_5)_2I : N(C_2H_5)_3]^+ \xrightarrow[S]{k_0} \rightarrow (C_6H_5)_2\dot{I}\overset{+}{N}(C_2H_5)_3 \xrightarrow{-C_6H_5I} C_6H_5\overset{+}{N}(C_2H_5)_3 \rightarrow \dot{C}_6H_5 + \dot{\overset{+}{N}}(C_2H_5)_3 \quad \text{(initiation)} \quad (5)$$

$$C_6\dot{H}_5 + (C_2H_5)_3N \xrightarrow[\text{slow}]{k_1} C_6H_6 + (C_2H_5)_2N-\dot{C}HCH_3$$
$$(C_6H_5)_2I^+ + CH_3\dot{C}H-N(C_2H_5)_3 \xrightarrow[-C_6H_5\cdot -C_6H_5I]{k_2}$$
$$\rightarrow CH_3\overset{+}{C}H-N(C_2H_5)_2 \longleftrightarrow CH_3CH=\overset{+}{N}(C_2H_5)_2$$
$$\downarrow$$
$$CH_2=CH-N(C_2H_5)_2 + H^+ \quad \text{(chain propagation)}$$

$$C_6\dot{H}_5 + \text{inhibitor} \xrightarrow{k_3} \text{inactive products (chain termination)}$$

Mechanism (5) explains the formation of benzene, biphenyl, and the triethylammonium salt on oxidation: it agrees with the formation of the compounds $RCH = \overset{+}{N}R_2$ or vinylamines, frequently observed in the oxidation of aliphatic amines (see below), and also with the formation of the radicals $CH_3\dot{C}HN.(C_2H_5)_2$ identified in the photochemical oxidation reaction[22].

The reaction with ethanolamine differs only by the fact that in the rate-limiting chain propagation stage the phenyl radical abstracts hydrogen not from a carbon atom of the amine but from the nitrogen atom to give the radical $\dot{N}HCH_2CH_2OH$, which participates in the chain propagation process.

On the other hand, the mechanism of the oxidation of dibutylamine differs significantly from mechanism (5)—the chain propagation is controlled by the second and not the first reaction:

$$C_6\dot{H}_5 + (C_4H_9)_2NH \xrightarrow{k_1} C_6H_6 + (C_4H_9)_2\dot{N} \ ;$$
$$(C_6H_5)_2I^+ + (C_4H_9)_2N^\cdot \xrightarrow[\text{slow}]{k_2} C_6\dot{H}_5 + PhI + (C_4H_9)_2\overset{+}{\dot{N}} \ . \quad (6)$$

This leads to the change in the kinetic equation already mentioned above.

The differences discussed are apparently caused by the fact that the radicals $(C_2H_5)_2N\dot{C}HCH_3$ and $\dot{N}HCH_2CH_2OH$ are less stable and are formed more slowly than the radicals

† The last equation was obtained from data for CIDNP kinetics in the benzene formed in the initiation stage. The addition of hydroquinone alters the form of the kinetic equation for the oxidation of dibutylamine; the mechanism of the effect of hydroquinone is obscure[19].

$(C_4H_9)_2\dot{N}$. On the other hand, it may be that the first two radicals give up their electrons to the iodonium cation more rapidly than $(C_4H_9)_2\dot{N}$, because the ionisation potential of the last radical is higher than those of the first two. This alters the ratio of the rates of the two chain propagation stages and the form of the kinetic equation.

The interaction of $(C_6H_5)_2I^+Cl^-$ with *N,N'*-tetramethyl-*p*-phenylenediamine (TMPA) [23] also obeys Eqn.(3) but differs radically from the three reactions considered. This is a radical and not a chain process. The CIDNP of the benzene formed is observed in the reaction, but there is no induction period and inhibitors of radical-chain reactions do not lead to its appearance and do not alter the rate of reaction. The reaction considered probably procceeds via a mechanism whose slow stage [and not the fast stage as in mechanism (5)] involves the formation of the complex

$$[(C_6H_5)_2I:N(CH_3)_2C_6H_4N(CH_3)_2]^+ \text{ (I) or CTC:}$$

$$(C_6H_5)_2I^+ + (CH_3)_2N{-}C_6H_4{-}N(CH_3)_2 \xrightarrow[\text{slow}]{} \text{(I) or CTC} \rightarrow$$

$$\rightarrow (C_6H_5)_2\dot{I}\,{}^{+}\left[(CH_3)_2N{-}C_6H_4{-}N(CH_3)_2\right] \xrightarrow{-C_6H_5I}$$

(II)

$$\xrightarrow{S} C_6\dot{H}_5\,{}^{+}\left[(CH_3)_2N{-}C_6H_4{-}N(CH_3)_2\right] \rightarrow C_6H_6 + \left[(CH_3)_2N{-}C_6H_4{-}N(CH_3)_2\right]^+ \quad (7)$$

However, one cannot rule out the possibility that the complex or the charge-transfer complex (CTC) are formed reversibly and that the homolytic decomposition of the complex or electron transfer in the CTC with formation of the pair (II) take place in the slow stage.

Reaction (7) is analogous to the initiation stage in mechanism (5) but, in contrast to mechanism (5), it is followed by the chain propagation stage. This can be explained by the fact that the radicals

$$\dot{N}(CH_3)\text{-}C_6H_4\text{-}N(CH_3)_2 \quad \text{or} \quad (CH_3)_2N\text{-}C_6H_3(\dot{C}HPh)\text{-}N(CH_3)_2,$$

which are probably formed when phenyl radicals interact with TMPA and which may be expected to be very stable, are incapable of transferring electrons rapidly to the Ph_2I^+ ions. This is why the chain propagation process cannot compete with reaction (7) as regards rate.

Thus the non-chain mechanism of the reaction considered is determined by the properties of the radicals formed from TMPA. It is clear from the foregoing that the properties of the radicals corresponding to amines determine the characteristics of the kinetics and mechanisms also of the other reactions considered.

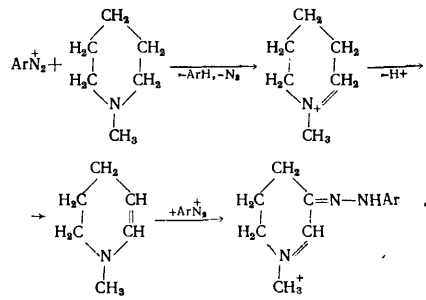
2. Oxidation by Diazonium Salts

The interaction of the salts $ArN_2^+BF_4^-$ with tertiary amines has been studied[25,26]. The reactions with tribenzylamine or benzyldimethylamine lead to the compounds ArH and immonium salts, which have been identified from the hydrolysis products. These results have been explained by the transfer of a hydride ion from the α-carbon atom to the ArN_2^+ ion:

$$ArN_2^+ + N(CH_2C_6H_5)_3 \xrightarrow[-ArH,-N_2]{} C_6H_5CH{=}\overset{+}{N}(CH_2C_6H_5)_2 \xrightarrow{+H_2O}$$

$$\rightarrow C_6H_5HO + (C_6H_5CH_2)_2NH + H^+ \quad .$$

N-Methyl- or *N*-benzyl-piperidine and *N*-benzylpyrrolidine react via a mechanism of the first type, which, however, is more complex



There are data in conflict with the above mechanism which indicate the involvement of radicals in the reactions. Thus the reaction induces the polymerisation of acrylonitrile[27] and is inhibited by oxygen and added bromotrichloromethane. A radical-chain mechanism was therefore proposed[28]:

$$ArN_2^+ + (RCH_2)_3N \rightarrow ArN{=}\dot{N} + (RCH_2)_3N^{\dot{+}};$$

$$ArN{=}\dot{N} \rightarrow A\dot{r} + N_2;$$

$$A\dot{r} + (RCH_2)_3N \rightarrow ArH + R\dot{C}HN(CH_2R)_2;$$

$$R\dot{C}HN(CH_2R)_2 + ArN_2^+ \rightarrow RCH{=}\overset{+}{N}(CH_2R)_2 + ArN{=}\dot{N}.$$

Unambiguous proof of the radical mechanism was obtained by Bilevich and coworkers[18,29-31]. They observed CIDNP in the benzene formed in the reactions of $PhN_2^+BF_4^-$ with aliphatic tertiary amines and the formation of the TMPA radical-cations and the polarisation of the protons of the substituted benzenes formed in the oxidation of TMPA by diazonium salts; the rate of the last reaction is proportional to the concentrations of both reactants. Substituents in the *para*-position in the ring of the salt alter by several orders of magnitude the rate of reaction (the oxidation is accelerated by the withdrawal of electrons by substitutents); the influence of the substituents obeys the Hammett equation ($\rho = 1.92$). The data presented served as the basis for the following mechanism of the slow stage:

$$ArN_2^+ + (CH_3)_2N{-}C_6H_4{-}N(CH_3)_2 \rightarrow ArN{=}\dot{N} + \left[(CH_3)_2N{-}C_6H_4{-}N(CH_3)_2\right]^{\dot{+}},$$

which includes electron transfer from the amine to the cation ArN_2^+.

The kinetics of the oxidation of trimethyl-, triethyl-, and tri-n-butyl-amines by the salts $p\text{-}XC_6H_4N_2^+BF_4^-$ have been investigated by Gragerov and coworkers[32,33] on the basis of the CIDNP kinetics in the compounds C_6H_5X formed. The reactions proved to be of the non-chain type and obeyed a first-order equation. Both electron-accepting and electron-donating substituents X accelerate the reaction by a factor of only 2–3 and the nature of the amine hardly affects its rate, although the basicities of the amines differ considerably.

The results differ sharply from those obtained by the oxidation of TMPA. To account for them, the authors assumed that the slow stage involves the decomposition into free radicals of the intermediate, possibly $Ar{-}N{=}N{-}\overset{+}{N}R_3$, formed via the mechanism

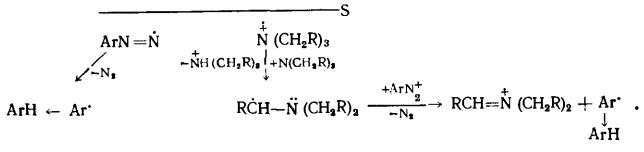
$$ArN_2^+ + R_3N \rightarrow Ar{-}N{=}N{-}\overset{+}{N}R_3 \quad .$$

This hypothesis is consistent with the first order of the reaction and explains the weak dependence of the reaction rate on the nature of X and the acceleration of the reaction by both electron-donating and electron-accepting substituents (these features are characteristic of many reactions involving decomposition into radicals—see, for example,

Walling[34]) and agrees with the independence of the rate of reaction of the nature of the amine.

The significant difference between the reactions of diazonium salts with TMPA and aliphatic tertiary amines is apparently caused by the stability of the TMPA radical-cations and the ease of electron transfer from TMPA. Thus, like the oxidation of amines by iodonium salts, it is caused by the nature of the radical species formed. The difference shows how unjustified can be a hypothesis concerning the details of the reaction mechanism arrived at by analogy.

The reactions of the radical pairs arising in the decomposition of the above intermediate can be represented schematically as follows:



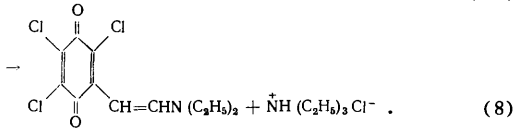
The presence of ammonium salts may be expected in the reaction products.

3. Oxidation by Quinonoid Compounds

The reactions of aliphatic tertiary amines with quinones have been investigated[35,36] and it has been found that, for example, triethylamine interacts with chloroanil in benzene via the mechanism

$$C_6O_2Cl_4 + (C_2H_5)_3N \rightarrow CH_2{=}CHN(C_2H_5)_2 + C_6H_2O_2Cl_2 \ .$$

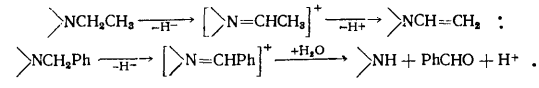
$$C_6O_2Cl_4 + CH_2{=}CHN(C_2H_5)_2 + (C_2H_5)_3N \rightarrow \qquad \text{(III)}$$



$$\qquad \text{(8)}$$

Other halogen-containing quinones react similarly, but the rate of reaction diminishes with decrease of the electron affinity of the quinone. Compounds of type (III) ("blue quinone") are formed only from amines containing the residue $\rangle NCH{-}CH_2{-}$. Amines with a different structure give rise to aldehydes among other products.

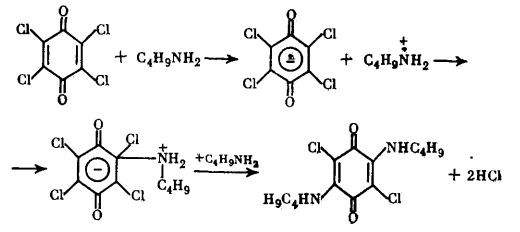
The authors[35,36] suggest that the key stage involves the transfer of a hydride ion from the amine to the quinone, which is followed rapidly by proton transfer from the β-position relative to the nitrogen atom. If there is no such proton in the molecule then the process stops at the stage involving the formation of immonium salts, whose hydrolysis gives rise to aldehydes:



A hydride ion is transferred in the CTC of quinones with amines. The existence of such complexes has been confirmed by spectroscopic data. The details of the hydride shift remain obscure.

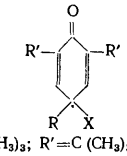
The above mechanisms involve the formation of semiquinone radical-anions preceding the formation of the "blue quinone". This was demonstrated by spectroscopic methods for reaction (8) in solution in chloroform or acetonitrile and the rate and activation energy and entropy for the formation of the semiquinone and compound (III) were determined[38]. The kinetic and activation parameters have also been obtained for electron transfer from tri-isopropylamine and tri-n-butylamine to chloranil. In these cases the process stops at the semiquinone radical-ion formation stage. In methanol or ethanol reaction (8) leads to trichlorohydroquinone and not to the "blue quinone"; the reason for this change has not been elucidated.

The formation of semiquinone radicals has been established in the interaction of quinones with amines of different structure. It is promoted by a low ionisation potential of the amine, a high electron affinity of the quinone, and a high solvent polarity[39]. These radicals proved to be intermediates in the nucleophilic substitution of quinones by amines[40]. In the first stages of the substitution reaction semiquinones accumulate and are then consumed as the products accumulate:



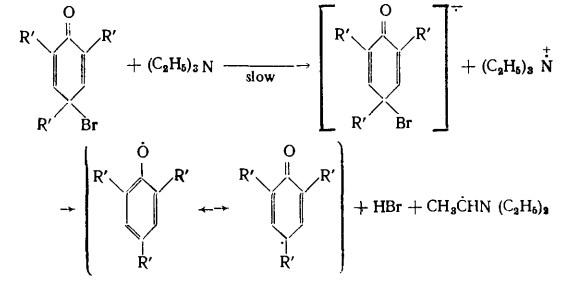
The reaction kinetics have been investigated.

The reactions of amines with other compounds having a quinonoid structure were investigated in a number of studies. Thus it has been established[41] that the reactions of sterically hindered quinobromides or quinonitrols



R=CH_3 or $C(CH_3)_3$; R′=$C(CH_3)_3$; X=Br or NO_2

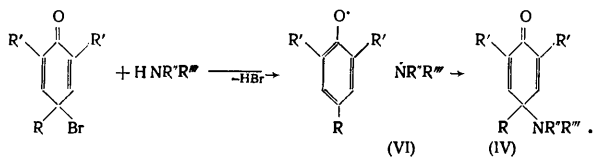
with triethylamine, piperidine, or pyridine give rise to phenoxy-radicals. The reaction in the presence of an excess of amines obeys a first-order kinetic equation; its rate and activation parameters have been found. It proceeds via the mechanism:



It has also been shown that the reaction of phenoxy-radicals with amines results in the formation of phenols.

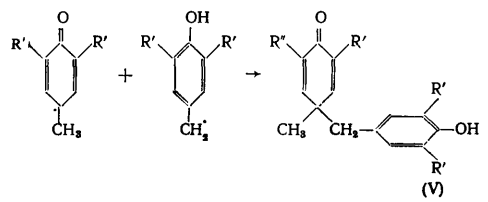
The reactions of the above quinobromides with primary and secondary amines have been investigated[42,43] and it has also been concluded that phenoxy-radicals are formed as intermediates. Apart from phenols and ammonium salts, the main products include quinamines (IV) and quinol (V). The reactions obey a second order kinetic equation and their rates and activation parameters have been found. The authors

believe that electron transfer from the amine to the quinobromide is the key stage in the processes:



(VI) (IV)

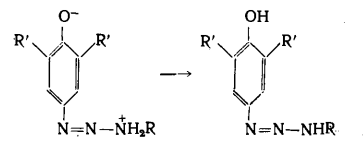
The formation of quinol (V) has been explained by the recombination of the phenoxy-radicals liberated from the pair (VI) with their isomerisation products[44]—hydroxybenzyl radicals:



(V)

The reactions of amines with *p*-benzoquinone diazides have been investigated. These reactions proceed rapidly with primary amines even at room temperature, giving rise to phenol, the quinone, and diphenoquinone corresponding to the quinone diazide used. The same products are obtained slowly in the reaction of quinone diazides with secondary amines or in the decomposition of the triazenes formed by the reaction of quinone diazides with secondary amines. Oxidation products are formed from amines, while with tertiary amines the reaction does not proceed.

The authors[45] suggest that triazenes are formed as intermediates. The triazenes corresponding to primary and secondary amines differ sharply in their stabilities. They are capable of decomposing into radicals (see, for example, Rozantsev and Sholle[46]). Radicals were indeed detected by EPR and with the aid of CIDNP. The CIDNP method made it possible to investigate their reaction pathways and thus to elucidate a series of details of the mechanisms of the processes[47,48]. The reaction mechanism taking into account all the data obtained is presented below in relation to the interaction of 2,6-di-t-butyl-*p*-benzoquinone diazide with primary amines (Scheme 1). Here the letters (A) and (E) denote positive and negative chemically induced nuclear polarisation, an asterisk represents a polarised atom, and (RP) is a radical pair (see below). The reaction begins with the addition of the electrophilic quinone diazide to the amine, which leads to the formation of a compound analogous to the product of the interaction of diazonium salts with tertiary amines (see above). Proton transfer to the oxygen results in the formation of a hydroxyphenyltriazene:



The nuclear polarisation in the latter indicates the reversibility of its decomposition and the sign of the polarisation in the azophenol (VIII) indicates its formation on disproportionation in $(RP_1)^S$. The sign of the polarisation shows that the main reaction product—the phenol (IX)—is formed mainly on disproportionation in $(RP_2)^S$.

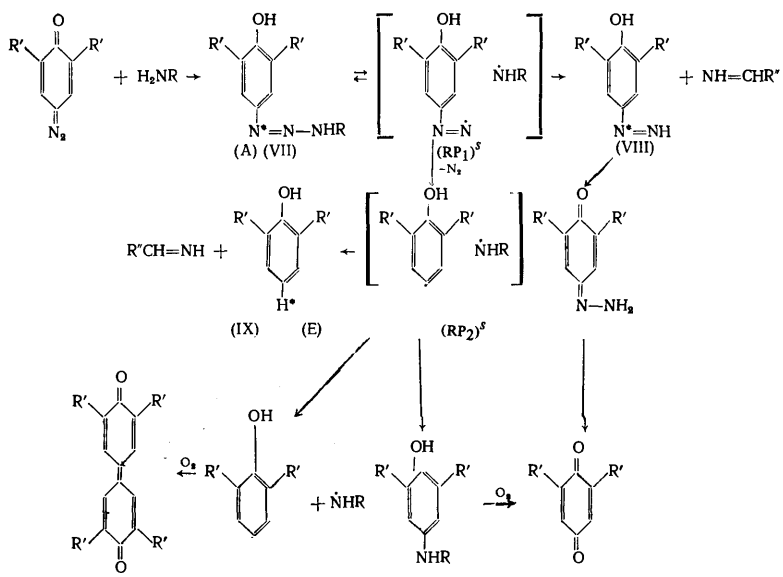
4. Oxidation with Chlorine Dioxide and Hypochlorous Acid

The oxidation of amines with chlorine dioxide in aqueous solutions has been studied[49–52]. Under conditions where side reactions are suppressed, two moles of ClO_2 are consumed per mole of the amine in the presence of an excess of the latter and amine dealkylation products and aldehydes are formed, for example:

$$(C_2H_5)_3N + 2ClO_2 + H_2O \rightarrow CH_3CHO + (C_2H_5)_2NH + 2H^+ + 2ClO_2^-$$

The rate is proportional to the amine and ClO_2 concentrations. It decreases in the sequence $(C_2H_5)_3N > (CH_3)_3N > (C_2H_5)_2NH$; the rate falls very rapidly on passing from tertiary to secondary and primary amines. The rates are correlated with the values of $\Sigma\sigma^*$ for the substituents at the nitrogen atom; $\rho = -5.24$. The rate constants for *meta*- and *para*-substituted benzyldimethylamines are satisfactorily correlated with

Scheme 1



the pK_a of the amines (the Brønsted parameter $\alpha = 0.812$) and with the σ constants ($\rho = -0.924$). The dealkylation is relatively unselective: formaldehyde and benzaldehydes are formed in proportions of ~3 : 1. The formation of amine radical-cations in the oxidation of $[(CH_3)_2N-C_6H_4-]_3N$ or $(CH_3)_2-C_6H_4-N(CH_3)_2$ was established by EPR.

The authors[49-52] suggest that the rate-limiting stage involves electron transfer from the amine to the oxidant with formation of ammonium radical-cations and ClO_2^- ions and not the abstraction of a hydrogen atom. This is confirmed by the finding that the $\Sigma\sigma^*$ for the residues at the nitrogen atom in secondary or tertiary amines are correlated not only with the rate of oxidation but also with the half-wave potential for the polarographic oxidation of amines, for which a similar mechanism is valid.

However, this mechanism does not account for all the observed features of the reaction. It has been shown that the addition of ClO_2^- ions diminishes the rate of oxidation without altering the kinetic equation and electron transfer is thus reversible. The decrease of the rate is proportional to the amounts of added ClO_2^- for $(C_2H_5)_3N$, $(CH_3)_3N$, and $[(CH_3)_2CH]_2NH$, but its dependence on the concentration of additives is more complex in the case of $C_6H_5CH_2NH_2$, $(C_6H_5CH_2)_2NH$, and $C_6H_5CH_2NHC(CH_3)_3$. Analysis of these relations leads to the conclusion that the last three amines react simultaneously via two mechanisms: with reversible electron transfer in the rate-limiting stage and with irreversible transfer of H^- from the α-carbon atom to the oxidant molecule in the slow stage of the reaction. The contribution of the reaction via the second pathway is 31% (at 41 °C) for $C_6H_5CH_2NHC(CH_3)_3$, 35% for $(C_6H_5CH_2)_2NH$, and 73% (at 25 °C) for $C_6H_5CH_2NH_2$. It is considerable for the amines under consideration because the C–H bonds in the CH_2 groups are weakened by the interaction with the benzene ring, and increases with increasing ionisation potentials of the amines, which hinders the competitive electron transfer. The transfer of H· in the slow stage was confirmed by the observation of primary kinetic isotope effects in the oxidation of $C_6H_5CD_2NHC(CH_3)_3$ and $C_6H_5CD_2NH_2$.

Thus amines which do not contain a CH_2 group next to the benzene ring react with ClO_2 by electron transfer in the slow stage:

$$ClO_2 + RCH_2N(R')R' \underset{}{\overset{\text{slow}}{\rightleftharpoons}} ClO_2^- + RCH_2\overset{+}{N}(R')R' \quad ;$$

$$RCH_2\overset{+}{N}(R')R' \xrightarrow{\text{fast}} H^+ + RCH{\cdots}N(R')R' \quad ;$$

$$RCH{\cdots}N(R')R' + ClO_2 \xrightarrow{\text{fast}} RCH{=}\overset{+}{N}(R')R' + ClO_2^- \quad . \qquad (9)$$

The proton elimination stage cannot be excluded from this mechanism and the latter cannot be replaced by

$$ClO_2 + RCH_2N(R')R' \underset{}{\overset{\text{slow}}{\rightleftharpoons}} ClO_2^- + RCH_2\overset{+}{N}(R')R' \quad ;$$

$$RCH_2\overset{+}{N}(R')R' + ClO_2 \xrightarrow{\text{fast}} HClO_2 + RCH{=}\overset{+}{N}(R')R' \quad ;$$

$$HClO_2 \rightleftarrows H^+ + ClO_2^- \quad ,$$

since analysis showed that the added ClO_2^- would infringe the first order of the reaction with respect to ClO_2 without the proton elimination stage, which is not observed.

Amines containing CH_2 groups linked to the benzene ring react with ClO_2 both via mechanism (9) and with transfer of H· in the slow stage:

$$ClO_2 + RCH_2N(R')R' \xrightarrow{\text{slow}} RCH{\cdots}N(R')R' + HClO_2 \rightleftarrows H^+ + ClO_2^- \quad ;$$

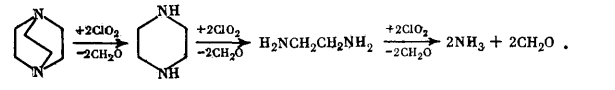
$$RCH{\cdots}N(R')R' + ClO_2 \xrightarrow{\text{fast}} RCH{=}\overset{+}{N}(R')R' + ClO_2^- \qquad (10)$$

Hydrolysis of the immonium salts formed via both mechanisms leads to the observed reaction products—the aldehydes RCHO and the amines R'_2NH.

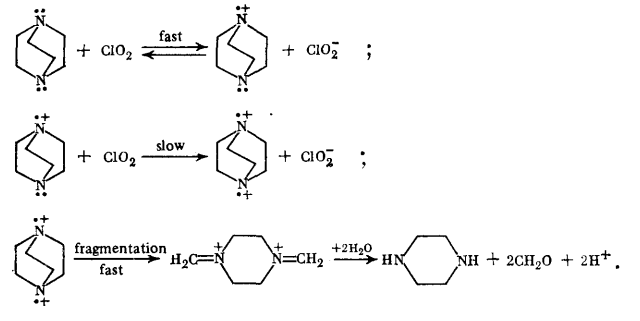
The results of Kudesia[53], who found that the replacement of water in the oxidation of benzylamine by D_2O (the replacement of $C_6H_5CH_2NH_2$ by $C_6H_5CH_2ND_2$) slows down the reaction by a factor of 5, are in conflict with the mechanisms described above and with experimental kinetic isotope effect data.

The amine dealkylation reactions under the influence of ClO_2 discussed above proceed with dissociation of C–N bonds. Reactions of another type, with dissociation of C–C bonds, are observed in the interaction of ClO_2 or HClO with β-amino-, β-hydroxy-, or β-oxo-amines, for example:

$$H_2NCH_2CH_2OH + 2ClO_2 \rightarrow NH_3 + 2CH_2O \quad ;$$



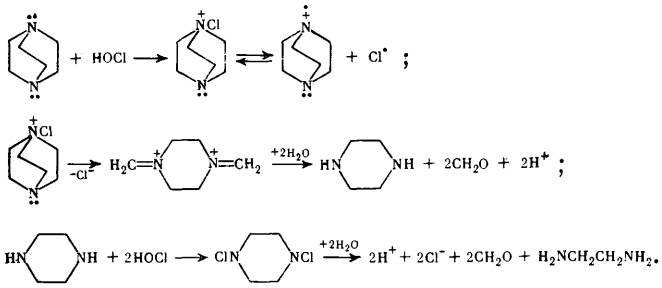
Such "oxidative fragmentation" has been studied[54-56] and the rate constants have been determined in many instances. The kinetics and mechanism of oxidative fragmentation have been investigated in relation to triethylenediamine. The reaction with this substance obeys a first-order kinetic equation with respect to the amine and a second-order equation with respect to the oxidant and is retarded by ClO_2^- ions in proportion to their concentration. The formation of triethylenediamine radical-cations in the course of the reaction has been demonstrated by EPR and the following mechanism has been proposed:



It involves the formation of the amine biradical-dication in the slow stage and not of a radical-cation as in mechanism (9). This difference is responsible for a change in the kinetic equation, which arises owing to the high stability of the triethylenediamine radical-cation. The triethylenediamine biradical-dication is unstable and rapidly fragments.

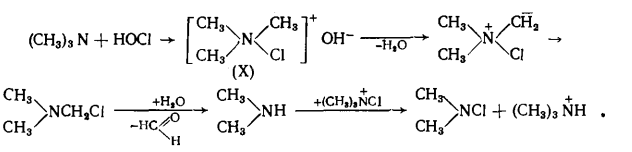
The oxidation of triethylenediamine by HOCl requires three moles of the acid per mole of the amine and probably obeys a first-order kinetic equation with respect to both the amine and the oxidant. Here too it was concluded that an ammonium radical-cation is formed in this reaction but the above investigators suggest that it is formed as a side product, since

HOCl is a two-electron oxidant. The mechanism is different:



The products contain 1,4-dichloropiperazine, since its hydrolysis is slow.

The oxidation of trimethylamine with HOCl in aqueous solutions gives rise to dimethylchloroamine and formaldehyde[57]:

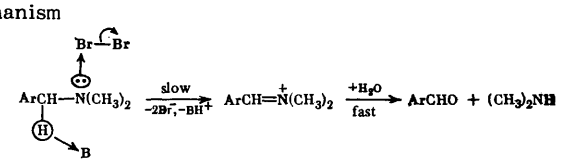


It proceeds via a mechanism analogous to mechanism (11). A proton is probably split off from compound (X) also in the reaction with the initial amine.

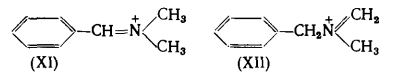
5. Oxidation with Bromine, Chlorine, and *N*-Halogenoamino-Compounds

The oxidation of amines with an aqueous solution of bromine at pH 5–7 in the presence of an excess of the amine has been studied[58]. Under these conditions, amines lose one alkyl group. Secondary alkyl groups are split off in the form of ketones and the fate of primary alkyls depends on the structure of the initial amine. The rate of oxidation of tripropylamine is proportional to the concentrations of both reagents, depends on pH in a complex manner, and is independent of illumination. The Hammett relation between the rate and the σ constants of the ring substituents holds for substituted benzyldimethylamines; $\rho = -0.84$. The reaction mechanism can consist in the elimination of an α-hydrogen atom in the form of H^+ with simultaneous abstraction of the electron pair at the nitrogen atom by the bromine. However, this mechanism does not account for the differences between the reaction products of primary, secondary, and tertiary amines. It has been confirmed and specified in greater detail by studies of the kinetics of the oxidation of *para*- and *meta*-substituted benzyldimethylamines with a bromine solution in 50% aqueous acetic acid[59].

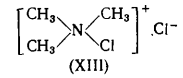
The reaction is of first order with respect to each reactant and its rate is correlated with the pK_a of the amines (the Brønsted parameter $\alpha = 0.67$) and obeys the Hammett relation ($\rho = -0.95$). The addition of sodium acetate or benzoate accelerates the oxidation; $C_6H_5CD_2N(CH_3)_2$ reacts more slowly than $C_6H_5CH_2N(CH_3)_2$. Irradiation with light does not affect the rate of reaction. The oxidation proceeds very selectively with formation of a high yield of benzaldehyde (in contrast to the radical oxidation of benzyldimethylamine with ClO_2). All these features of the reaction can be accounted for by the mechanism



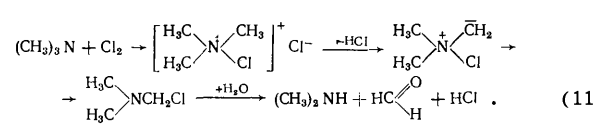
(where B is a base). The selectivity of the oxidation is associated with the preferential formation in the limiting stage of the ions (XI), which, in contrast to the ions (XII), are stabilised by the conjugation of the C=N bond with the ring:



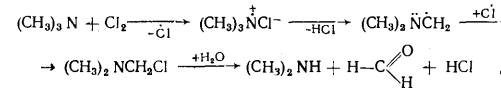
When trimethyl- or triethyl-amine interacts with an aqueous solution of an equimolar amount of chlorine, the hydrochloride of the corresponding secondary amine is formed. In solution in CCl_4, trimethylamine forms with chlorine a compound which probably has the following structure:



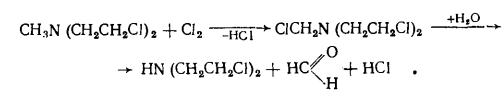
On hydrolysis, this compound is converted into the products formed on reaction of trimethylamine with an aqueous chlorine solution. On this basis, the following heterolytic mechanism has been proposed[60]:



However, it has been shown[61] that mechanism (11) is not consistent with the kinetic data and that compound (XIII) or the reaction mixture in the interaction of trimethylamine with chlorine cause the polymerisation of acrylonitrile. The authors[61] therefore propose the radical mechanism



The oxidation of amines of the type $RN(CH_2CH_2Cl)_2$ with chlorine and *N*-chloroimides, leading to the dealkylation of the amine, has been studied[62], for example:



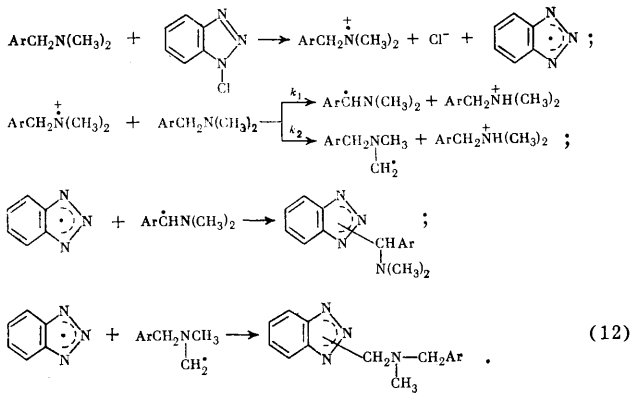
The reaction mechanism was not investigated.

The oxidation of amines by 1-chlorobenzotriazole has been investigated[63]. In the case of *para*-substituted benzyldimethylamines the reaction leads to 1- and 2-aminoalkylbenzotriazoles, the hydrochlorides of the initial amines, and compounds containing active (positive) chlorine. The rate of formation of products, not containing active chlorine, in benzene is proportional to the concentrations of both reactants and is correlated with the pK_a of the amines (the Brønsted parameter $\alpha = 0.63$). The influence of substituents in the benzene rings of the amines is described by the Hammett equation ($\rho = -0.71$). An induction period is not observed in the reaction and its rate is independent of illumination and the presence of oxygen or radical-chain process inhibitors. $C_6H_5CH_2N(CH_3)_2$ is oxidised faster than $C_6H_5CD_2N.(CH_3)_2$. The reaction is accelerated by the addition of methanol. *para*-Substituted benzaldehydes, p-$XC_6H_4CH_2.NHCH_3$ and formaldehyde, formed from aminoalkylbenzotriazoles, were identified after acid hydrolysis.

The oxidation of triethylenediamine yields 1,4-bis(benzotriazolylmethyl)piperazine—the product of the oxidative fragmentation of the amine. It has been established by EPR

that ammonium radical-cations are formed in the reaction. The radical-cations have been identified also in the oxidation of *N,N'*-tetramethyl-*p*-phenylenediamine. Primary amines give rise to monochloroamines.

The formation of aminoalkylbenzotriazoles has been explained by a radical non-chain mechanism, which agrees with all the data described above:



(12)

The authors[63] rejected two variants of the ionic mechanism—with transfer of H^- or Cl^+—on the grounds of not very reliable criteria—the inconsistency of the values of ρ and the kinetic isotope effects with values usually observed for such mechanisms.

The ratio of the yields of the hydrolysis products of aminoalkylbenzotriazoles, namely substituted benzaldehydes and p-$XC_6H_4CH_2NHCH_3$, is determined by the rates of abstraction of H^+ from the CH_2 or CH_3 groups of the ammonium radical-cations and is equal to the ratio k_1/k_2 [see mechanism (12)]. This mechanism depends on the nature of X and decreases with increasing solvent polarity. For reactions in methanol, it is close to the statistical value, as in the oxidation of benzyldimethylamines by a solution of ClO_2 in water.

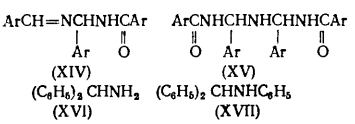
When tertiary amines are acted upon by *N*-bromosuccinimide, the C–N bonds are broken and secondary amines and aldehydes are formed (see, for example, Dunstan and Henvest[64] and Filler[65]). A radical mechanism has been proposed for the reaction on the basis of general considerations[66].

Studies on the oxidation of amines by "chloramine-T" ($CH_3C_6H_4SO_2NNaCl$) have been undertaken for synthetic purposes. The problems of the reaction mechanism have been investigated only in relation to diethanolamine[67] and monoethanolamine[68]. Both compounds undergo oxidative fragmentation with formation of formaldehyde, formic acid, and ammonia. The details of the mechanism are obscure.

6. Oxidation with Potassium Permanganate, Periodic Acid, and Chromic Acid

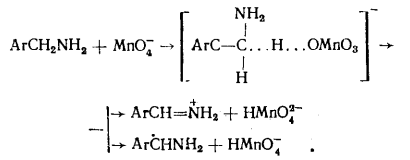
The mechanism of the oxidation of amines by potassium permanganate has not so far been thoroughly elucidated. A brief review of early studies has been published[69]; the investigations in recent years are considered below.

Substituted benzylamines give rise to compounds (XIV) and (XV) on oxidation with $KMnO_4$ in a 1 : 1 aqueous t-butyl alcohol in the presence of an excess of $CaSO_4$:



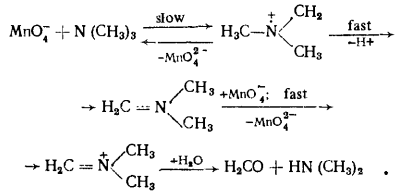
The reaction mechanism has not been established, but the aldimines ArCH=NH are probably formed in the initial stages; the initial amines then add to them, giving rise to products whose oxidation leads to compounds (XIV) and (XV).[72] The oxidation of compound (XVI), dibenzylamines, and compound (XVII) apparently proceeds similarly. Tertiary amines, incapable of being converted into aldimines, are oxidised differently. Thus tributylamine gives rise to dibutylamine, butyraldehyde, butyric acid, and the *N,N*-dibutylamide of butyric acid, which are products of subsequent interactions of the enamine $(C_4H_9)_2NCH{=}CHCH_2CH_3$ formed initially. Tribenzylamine is oxidised to benzaldehyde and benzoic acid; dibenzylamine is not formed. The mechanism of this reaction has not been established[70].

It has been observed[71] that in the reaction of substituted benzylamines with $KMnO_4$ in water, the amines and not their salts are oxidised. At pH 10 the rate of reaction is described by a first-order equation with respect to the amine and the oxidant. The rate is independent of the ionic strength of the solution. The activation energy and entropy are 10.4–11.7 kcal mol^{-1} and from −21.6 to −24.8 e.u. respectively. Benzylamine is oxidised seven times faster than $C_6H_5CD_2NH_2$ but at the same rate as $C_6H_5CH_2ND_2$. The influence of substituents is correlated with σ^+ ($\rho = -0.28$). At high pH yet another reaction takes place whose mechanism has not been established. The following mechanism has been proposed for the reaction in weakly alkaline media:



Here the activated complex decomposes with transfer of a hydride ion or H·. The radicals are then (after the loss of the proton) oxidised to benzaldimine.

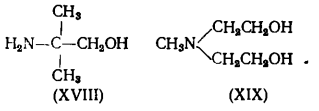
It has been found[73] that the rate of oxidation of amines at pH 7.5–8 is proportional to the concentration of the oxidant and the substrate and decreases in the sequence $(C_2H_5)_3N$ > $(C_2H_5)_2NH$ > $C_2H_5NH_2$; it has also been found that $(CH_3)_3N$ is oxidised to formaldehyde 1.84 times faster than $(CD_3)_3N$. According to the authors[73], an electron is transferred in the slow stage of the oxidation of trimethylamine and the abstraction of hydrogen is not the main reaction pathway. The reaction proceeds preferentially via a mechanism analogous to that of the oxidation by ClO_2:



On passing to secondary or tertiary amines, the abstraction of hydrogen in the slow reaction stage assumes increasing importance, as in the oxidation by ClO_2.

The oxidation of $(CH_3)_3N$ and $(C_2H_5)_3N$ with aqueous $KMnO_4$ at pH 6–8 has been studied[74] and a mechanism has been proposed in which the ammonium radical-cations are formed when amines interact with manganese complexes. The latter are obtained in the first stages from complexes of the amines with manganese (VII) and manganese(V) compounds.

On treatment with periodic acid; ethanolamine, diethanolamine, triethanolamine, ethylenediamine, and the amines (XVIII) and (XIX) undergo oxidative fragmentation[75], the reactions with ethanolamine and ethylenediamine being quantitative[76].



(XVIII) (XIX)

The study of the kinetics of the oxidation of ethanolamine[77] and *N*-methylethanolamine[77,78] did not yield sufficient data for the determination of the reaction mechanism. It is not even clear whether ethanolamine or their protonated forms and which of the ions $H_4IO_6^-$ and $H_3IO_6^{2-}$, $H_2IO_5^-$, or HIO_5^{2-} are involved in the reaction.

The mechanism of the oxidation of amines with chromic acid has not been studied. Data on the kinetics of the oxidation of a number of amines to CO_2, H_2O, and NH_3 by $K_2Cr_2O_7$ in an acid medium have been published in only one communication[79].

7. Oxidation by $K_3Fe(CN)_6$, $Pb(OCOCH_3)_4$, Silver(II) Picolinate, and $AgNO_3$

Smith and coworkers studied the oxidation of tertiary amines by $K_3Fe(CN)_6$ in aqueous solutions at pH > 12. In the presence of an excess of the substrate, two moles of the oxidant are consumed per mole of the amine and mainly oxidative dealkylation products are formed. The reaction obeys a first-order kinetic law with respect to the oxidant and the amine. Tertiary *N*-methyl- and *N*,*N*-dimethyl-amines are mainly demethylated[80]. The secondary amines formed are not oxidised further. The rate of reaction is correlated with the $\Sigma\sigma^*$ of the substituents at the nitrogen atom; $\rho^* = -5.45$ and is close to $\rho^* = -5.24$ found for the oxidation of amines by ClO_2, where an electron is transferred in the rate-limiting stage. The addition of $K_4Fe(CN)_6$ does not affect the rate of oxidation. The salt effect of cations is observed. All these data can be accounted for by a mechanism involving the irreversible transfer of an electron from the amine to the oxidant in the slow stage#:

$$RCH_2NR'_2 + Fe(CN)_6^{3-} \xrightarrow[-Fe(CN)_6^{4-}]{slow} RCH_2\overset{+}{N}R'_2 \xrightarrow{-H^+}$$

$$\rightarrow RCH{=}NR'_2 \xrightarrow[-Fe(CN)_6^{4-}]{+Fe(CN)_6^{3-}} RCH{=}\overset{+}{N}R'_2 \xrightarrow{+OH^-}$$

$$\rightarrow RCH(OH)NR'_2 \rightarrow RCHO + R'NH \quad . \qquad (13)$$

An alternative mechanism, in which the first two stages have been replaced by the concerted loss of an electron and an α-proton by the amine, i.e.

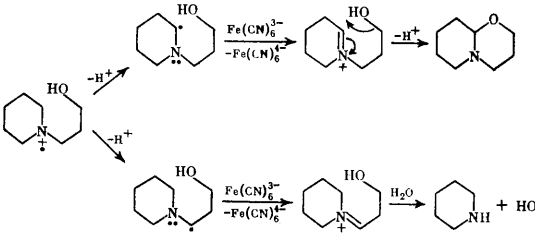
$$RCH_2NR'_2 + Fe(CN)_6^{3-} \rightarrow R\dot{C}HNR'_2 + Fe(CN)_6^{4-} + H^+ \ ,$$

is in poor agreement with the high value of ρ^* and the small kinetic isotope effect (see below). The possibility of the simultaneous occurrence of the reaction via both mechanisms is ruled out by the finding that a linear relation between $\delta\Delta H^{\neq}$ and $\delta\Delta S^{\neq}$ holds for a series of the amines investigated.

It has been found[82] that at pH 8.8 the rate of oxidation of triethylamine by $K_3Fe(CN)_6$ diminishes following the addition of $K_4Fe(CN)_6$ in proportion to the concentration of the additive. It was therefore concluded that the electron transfer in the slow stage is reversible. The discrepancy between these data and the findings described above was explained by differences in the pH.

The oxidation of *para*-substituted benzyldimethylamines[81] also proceeds via mechanism (13). The rate of reaction is correlated with the Hammett σ constants of the ring substituents, with the $\Sigma\sigma^*$ of the substituents at the nitrogen atom, and with the pK_a of the amines. The values of ρ, ρ*, and α (−0.989, −4.24, and 0.990 respectively) are close to those found for the oxidation of benzyldimethylamines by ClO_2. The ratio of the demethylation and debenzylation products (formed after the loss of H^+ from the CH_3 or CH_2 group in the amines) differs from the statistical ratio. According to mechanism (13), it is determined by the relative acidity of the *N*-methyl or *N*-benzyl hydrogen atoms and the number of these atoms.

Mechanism (13) has been confirmed in the oxidation of trialkylaminoalcohols and trialkylaminoamines[83]. Thus 3-piperidino-1-propanol gives rise to a cyclisation product and piperidine, which can be explained by the intermediate formation of a radical-cation and of immonium ions:



The electron transfer in the rate-limiting stage is confirmed by the low kinetic isotope effect in the oxidation of $CH_3N(C_4H_9)_2$ and $CD_3N(C_4H_9)_2$ ($k_H/k_D = 1.04$). The ratio of the demethylation and debutylation products changes greatly on isotope substitution—the isotope effect is 3.6.[84]

It has also been shown[84] that the characteristics of the rate of oxidation of tertiary amines with a nitrogen atom in the ring or bicyclic tertiary amines can be satisfactorily explained by mechanism (13). The radical-cations $R_3\overset{+}{N}$ have a planar structure and the transition state for their formation is a structure close to that of radical-cations. The rate of oxidation is therefore controlled by the changes in ring strain and the barriers to changes in conformation which arise when the molecules are converted into radical-cations. This treatment has been confirmed[85] in relation to trialkylaminoalcohols, their ethers, trialkylaminoamines, phenetylamines, and cyclic, bicyclic, and tricyclic amines.

In contrast to tertiary amines, diethanolamine undergoes oxidative fragmentation in oxidation by $K_3Fe(CN)_6$ in aqueous alkali[86–88]:

$$NH(CH_2CH_2OH)_2 + 4OH^- + 4Fe(CN)_6^{3-} \rightarrow 4HCHO + \\ + NH_3 + 4Fe(CN)_6^{4-} + 2H_2O \quad .$$

The process is analogous to the oxidation of β-hydroxyamines by ClO_2, but its mechanism has been studied inadequately. At low $K_3Fe(CN)_6$ concentrations the rate of oxidation is proportional to the concentrations of alkali, the substrate, and the oxidant, but the reaction order with respect to the oxidant decreases with increasing concentration of the latter and may become zero. The addition of salts, including $K_4Fe(CN)_6$, accelerates the reaction, while the addition of methanol retards it. The following mechanism has been proposed:

$$NH(CH_2CH_2OH)_2 + OH^- \underset{-H_2O}{\rightleftharpoons} HOCH_2CH_2NHCH_2CH_2O^- \xrightarrow{+Fe(CN)_6^{3-}}$$

$$\rightarrow complex \xrightarrow{+Fe(CN)_6^{3-}} 2Fe(CN)_6^{4-} + products.$$

At low oxidant concentrations the rate of reaction is limited

by the formation of a complex, which explains the third order of the reaction, while at high oxidant concentration it is limited by the ionisation of ethanolamine.

The oxidation of primary amines with a methylene group by $Pb(OCOCH_3)_4$ in boiling benzene[89,90] leads to the formation of nitriles in yields up to 60%. The reaction is believed to be a two-stage dehydrogenation process with the intermediate formation of aldimines. The mechanism has been confirmed by the formation of 2–4% of benzaldehyde in the oxidation of benzylamine and subsequent hydrolysis, since the aldehyde is probably formed from the aldimine $C_6H_5CH{=}NH$. Aliphatic aldehydes are not formed in the reaction, since their aldimines are unstable. They rapidly polymerise, which lowers the yield of nitriles and increases the yield of resins.

In specifying the details of the mechanism, the authors[89,90] postulated the intermediate formation of the products (XX) and (XXI) of the aminolysis of lead tetra-acetate [see mechanism (14)] and their homolytic decomposition. This is based on the analogy with the alcoholysis of $Pb(OAc)_4$ and the photochemical oxidation of benzylamine to benzonitrile by $Pb(OAc)_4$. The reaction mechanism is as follows:

$$RCH_2NH_2 + Pb(OAc)_4 \overset{a}{\rightleftarrows} RCH_2NHPb(OAc)_3 + AcOH$$
$$\overset{c}{\downarrow} \qquad \overset{b}{\downarrow} \quad (XX)$$
$$RCH_2\dot{N}H + \dot{P}b(OAc)_3 \rightarrow RCH{=}NH + Pb(OAc)_2 + AcOH \ ;$$

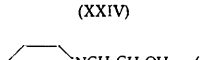
$$RCH{=}NH + Pb(OAc)_4 \overset{a}{\rightleftarrows} RCH{=}NPb(OAc)_3 + AcOH$$
$$\overset{c}{\downarrow} \qquad \overset{b}{\downarrow} \quad (XXI)$$
$$RCH{=}\dot{N} + \dot{P}b(OAc)_3 \longrightarrow RC{\equiv}N + Pb(OAc)_2 + AcOH \ . \qquad (14)$$

Compounds (XX) and (XXI) are converted into an imine or a nitrile either directly (pathway *b*) or with the intermediate formation of radical pairs (pathway c). Mechanisms involving the formation of side products have also been proposed.

The oxidation of dibenzylamine gives rise to benzaldehyde, benzonitrile, benzylamine, and the compounds $C_6H_5CH_2N = CHC_6H_5$ (XXII) and $C_6H_5CH(COCH_3)NH = CHC_6H_5$ (XXIII). A reaction mechanism has been proposed in which compound (XXII) is formed in the first stage via a mechanism analogous to mechanism (14); its subsequent reactions explain the formation of the other products mentioned.

Triethylamine is very slowly oxidised by lead tetra-acetate in glacial acetic acid, while the amines (XXIV)–(XXVII) are rapidly oxidised. After hydrolysis, the amines (XXIV)–(XXVI) give high yields of diethylamine, while compound (XXVII) gives rise to piperidine. The hydroxylamines (XXVIII) and (XXIX) are oxidised much more slowly than compounds (XXIV)–(XXVII) but faster than the mixture of $(C_2H_5)_3N$ and 1-propanol, which is in its turn oxidised faster than triethylamine[91]. The oxidation of the amines (XXIV) and (XXVII) results in the formation of glyoxal.

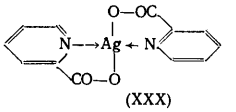
$(C_2H_5)_2NCH_2CH_2OH$ (XXIV); $(C_2H_5)_2NCH_2CHCH_3$ (OH) (XXV); $(C_2H_5)_2NCH_2C(CH_3)_2$ (OH) (XXVI);


(XXVII); $(C_2H_5)_2NCH_2CH_2CH_2OH$ (XXVIII); $(C_2H_5)_2NCH_2CH_2CH_2CH_2OH$ (XXIX) .

The above data show that the C–N bonds are cleaved in the reaction. The authors quoted above proposed the following process mechanism:

$$(C_2H_5)_2NCH_2CH_2OH \xrightarrow[-CH_3COOH]{+CH_3COO^-} (C_2H_5)_2N\dot{C}HCH_2OH \xrightarrow{+CH_3COO^-}$$
$$\rightarrow (C_2H_5)_2NCH(OCOCH_3)CH_2OH \xrightarrow{+H_2O} (C_2H_5)_2NH + CH_3COOH + O{=}CHCH_2OH$$

The oxidation of primary and secondary amines with an α-hydrogen atom by a suspension of silver(II) picolinate (XXX) in water or polar solvents[93] leads to the formation of aldehydes or ketones and apparently proceeds via an imine formation stage.


(XXX)

The imines were isolated in those instances of the oxidation of secondary amines where the imines were stable. Stable imines, corresponding to primary amines, are oxidised further to nitriles. The stoichiometry of the reaction is described by the equations

$$\rangle CHNH_2 + 2Ag^{2+} + H_2O \rightarrow \rangle CO + NH_3 + 2Ag^+ + 2H^+ \ ;$$
$$\rangle CHNHR + 2Ag^{2+} \rightarrow \left(\rangle C{=}NR + 2Ag^+ + 2H^+\right) \overset{H_2O}{\rightleftarrows} \rangle CO + RNH_2 + 2Ag^+ + 2H^+ \ .$$

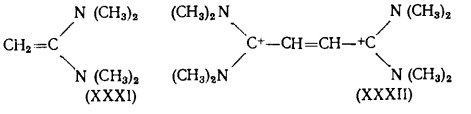
The authors[93] suggest that the amines substitute picolinic acid in the complex (XXX), after which they give up an electron to silver(II). This is followed by the oxidation of the resulting radical by a second picolinate molecule, which leads to an imine either directly or via a hydroxyamine formation stage:

$$RCH_2NHR' \rightarrow Ag(I) + RCH_2\overset{+}{N}HR' \rightarrow R\dot{C}HNHR' + H^+ \ ;$$
$$\downarrow Ag(II)$$
$$Ag(II) + R\dot{C}HNHR' \begin{cases} \longrightarrow Ag(I) + H^+ + RCH{=}NR' \\ \xrightarrow{H_2O} Ag(I) + H^+ + RCH(OH)NHR' \rightleftarrows RCHO + R'NH_2 \ . \end{cases}$$

One cannot rule out the possibility that imines are formed in the disproportionation of α-amino radicals:

$$2R\dot{C}HNHR' \rightarrow RCH{=}NR' + RCH_2NHR' \ .$$

The interaction of vinylidenebisdialkylamines with silver nitrate in acetonitrile leads to oxidative dimerisation with formation of diamidinium salts[94,95]. Thus compound (XXXII) and metallic silver are formed from compound (XXXI).


(XXXI) (XXXII)

If the initial amine contains two double bonds, there is a possibility of the formation of cyclic or bicyclic products. It has been suggested that the reaction proceeds with participation of radical-cations. In certain cases their formation was established by EPR.

8. Oxidation with Molecular Oxygen and Ozone

When triethylamine is oxidised with oxgen in the gas phase at 200 °C,[96,97] mainly ethylamine, acetaldehyde, and diethylamine are formed. The diethylamine concentration initially increases, but rapidly attains a limiting value. It has been suggested that oxygen abstracts H˙ from the CH_2 group, after which another oxygen molecule adds to the resulting radical to form a peroxy-radical; ethylamine is formed in the intramolecular decomposition of this radical, while diethylamine arises in consequence of the decomposition of the hydroperoxide. The details of the mechanism have not been determined.

The kinetics of the radical-initiated liquid-phase oxidation of amines by oxygen have been studied[98–109]. These reactions proceed at a lower temperature than the gas-phase

oxidation, but their products have not been investigated. In most cases the oxidation involves radical-chain processes and proceeds via the following mechanism with both primary and secondary amines:

$$\text{Initiator} \xrightarrow{+RH,+O_2} \dot{R} \xrightarrow{+O_2} R\dot{O}_2 \xrightarrow{+RH} ROOH + \dot{R} \quad ;$$
$$2R\dot{O}_2 \rightarrow O_2 + \text{molecular products.}$$

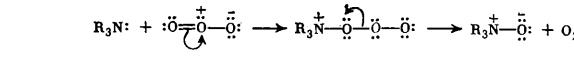
Here $\dot{R}$ = α-amino-radical. Tertiary amines are oxidised more readily than primary and secondary amines. The involvement of enamines in the reaction and in certain cases linear chain termination have been postulated[102].

The specific features of the reactions consist in the fact that α-aminoperoxy-radicals have not only oxidative but also reductive properties. They are capable of regenerating the inhibitors of radical-chain processes, which explains the observed high stoichiometric inhibition coefficients.

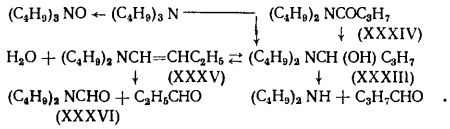
The liquid-phase autoxidation of enamines with a complex structure has been studied[110]. The reaction proceeds via a radical-chain mechanism. In the initiation stage the amine gives up an electron to the oxygen with formation of ammonium radical-cations. The Fe^{3+} and Cu^{2+} ions react similarly and greatly accelerate the autoxidation.

It has been found[111] that $RuCl_3$ catalyses the homogeneous liquid-phase oxidation of amines by oxygen. In toluene at 100 °C benzylamine is converted into benzonitrile and benzamide, while butyronitrile and butyramide are formed from n-butylamine. 2-Aminohexane gives rise to the corresponding ketone (formed in the hydrolysis of the imine) and the product of the condensation of the ketone with the initial amine. Variants of the mechanism involving ruthenium(III)—amide and ruthenium(III)—hydride complexes have been proposed.

In their interaction with ozone in chloroform at low temperatures, tertiary amines are converted with high yields into *N*-oxides[112]. The reaction probably proceeds via the mechanism[112,113]



The reaction has been studied in detail in relation to tri-n-butylamine[6,114]. Apart from its *N*-oxide, compounds (XXXIV) and (XXXVI) and dibutylamine are formed. The ratio of their yields is influenced by the nature of the solvent and temperature. In chloroform or methanol at −45 °C the main product is the *N*-oxide, while in hydrocarbons or 1-chlorobutane the products are dibutylamine at −45° or −78 °C and compound (XXVI) at +15 °C. It has also been shown that, for a tributylamine : ozone ratio of 1 : 1 at −78 °C in pentane, subsequent heating to 20 °C results in the formation of the enamine (XXXV), which is oxidised by ozone to compound (XXXVI). The following process mechanism has been proposed:



The formation of an *N*-oxide is apparently favoured by the tendency of the solvent to form hydrogen bonds; the carbinolamine (XXXIII) is obtained in solution in hydrocarbons or 1-chlorobutane. It is oxidised to compound (XXXIV), hydrolyses to butylamine and butyraldehyde, and is dehydrated to compound (XXXV) with subsequent ozonolysis at the double bond. Heating, which promotes dehydration, lowers the yield of dibutylamine and increases that of dibutylformamide. Hydrolysis of the carbinolamine, leading to dibutylamine and butyraldehyde, predominates in the oxidation of a suspension of tributylamine in water. The mechanism discussed does not, however, explain the formation of carbinolamine.

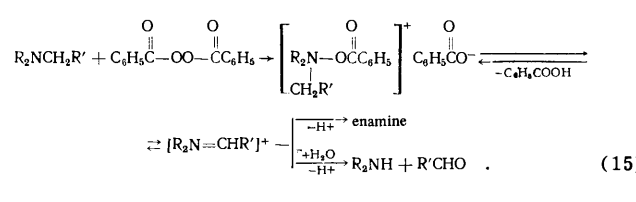
Primary amines are oxidised by ozone to nitro-compounds. At low temperatures the yields are 25–50%.[115] Alkylhydroxyamines and nitroso-compounds are probably formed initially, which is confirmed by the presence in the reaction mixture of alkylhydroxylamines when the oxidation is interrupted, after the introduction of one equivalent of ozone, by the conversion of alkylhydroxylamines into nitro-compounds under the influence of ozone and by the colour characteristic of nitroso-compounds appearing in the course of the reaction.

Since oximes are not converted into nitro-compounds on being oxidised with ozone, it is to be expected, in conformity with the mechanism discussed, that amines with tertiary hydrocarbon groups, which are converted into nitroso-compounds incapable of isomerising to oximes, would give rise to higher yields of nitro-compounds than amines with primary or secondary hydrocarbon groups. This prediction has been confirmed. However, it is noteworthy that the mechanism of the formation of alkylhydroxylamines and of their conversion into nitroso-compounds and then nitro-compounds remains obscure.

9. Oxidation by Peroxy-Compounds

The oxidation of amines by peroxy-compounds frequently depends on the nature of the solvent and the mechanism is often different for primary, secondary, and tertiary amines. These reactions apparently include both heterolytic and homolytic processes. The study of their kinetics is complicated by the inhibition or acceleration of the oxidation by reaction products, which is frequently encountered, and by the widespread occurrence of radical-chain processes. The oxidation mechanisms are by no means always satisfactorily justified and their details are frequently unknown.

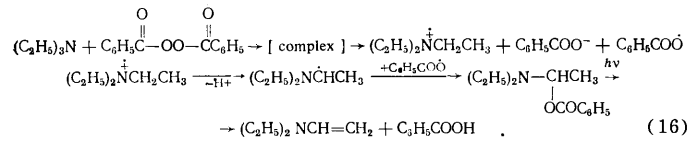
The interaction of benzoyl peroxide with tertiary amines has been investigated[116]. In benzene, in the presence of an excess of the amine, the stages involving the oxidation of amines with the $R_2NCH_2CH_2$ group yield enamines, which have been identified from the formation of compounds of the "blue quinone" type (see Section III, 2) when the reaction is carried out in the presence of quinones. The enamine $(C_2H_5)_2.NCH{=}CH_2$ has been isolated[117]. Amines of the type $(CH_3)_2.NCH_2Ar$, which are incapable of forming enamines, give rise to immonium salts, which hydrolyse to secondary amines and carbonyl compounds. These data can be accounted for by a mechanism analogous to that of the interaction of benzoyl peroxide with dimethylaniline[118]:



(15)

The first stage involves nucleophilic substitution with formation of a quaternary salt, corresponding to the ether of the substituted hydroxylamine. Mechansim (15) has been confirmed by the isolation of a compound of this type in the oxidation of triethylamine by acetyl peroxide[119]; however, it conflicts with the formation of radicals giving rise to polymerisation (see, for example, Margaritova and coworkers[120,121]).

The involvement of radicals in the stages where amines are oxidised by benzoyl peroxide, the intermediates, and the kinetics and mechanisms of the reactions have been investigated[122-128]. The authors used a method based on the chemiluminescence which arises in the course of the recombination of radicals: its appearance is a sign of a radical mechanism and the variation of its intensity makes it possible to infer the reaction kinetics. It has been established that the oxidation of triethylamine by benzoyl peroxide obeys a first-order kinetic equation with respect to each reactant and has a radical but not chain mechanism. Benzoic acid retards while pyridine accelerates the reaction as a result of the formation of complexes with the amines or the peroxide respectively. In the presence of an excess of the peroxide, chemiluminescence, corresponding to the oxidation of an intermediate, probably an enamine, is observed. On hydrolysis, the enamine gives rise to diethylamine and acetaldehyde. The following mechanism has been proposed:



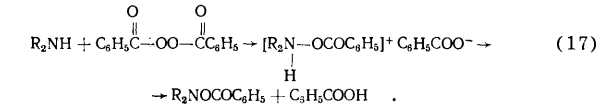
(16)

It is closer to Horner's mechanism of the oxidation of *N*,*N*-dialkylanilines (see, for example, Horner and Junkermann[129]). It may be that the intermediate complex is a quaternary salt, corresponding to an ether of the substituted hydroxylamine[130], which rapidly decomposes into radicals. It is also possible that the salt decomposes simultaneously via a non-radical mechanism (see, for example, Walling and Inductor[117]).

According to the authors of the studies quoted, the oxidation of aminoalcohols $R'R''NCH_2CH_2OH$ [123,128,131] proceeds via a mechanism analogous to mechanism (16). The oxidation of triethanolamine[132-134] is a radical-chain reaction.

The structure factors which determine the mode of dealkylation of tertiary amines have been studied[135].

The secondary amine oxidation reactions[122,126,127,133,136-140] are also usually second-order reactions. Radicals are probably not formed in these reactions or not in the initial stages, being produced in the oxidation of the intermediates [for example, of $(C_2H_5)_2NCH{=}CH_2$, obtained in the oxidation of diethylamine[143]]. The radical mechanisms proposed previously (see, for example, Horner and Kirmse[194]) are probably incorrect[142]. Apparently the cations of the quaternary salts obtained from hydroxylamine derivatives are formed in these reactions and then rapidly lose protons:

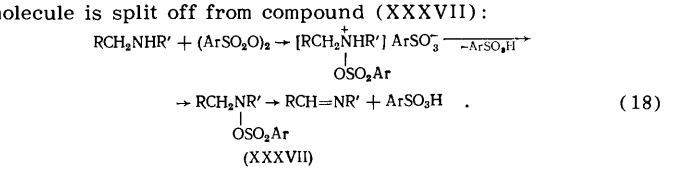


(17)

Nor can one rule out the possibility[139] that secondary amines react with an amine–peroxide complex rather than the peroxide itself.

The oxidation of primary amines by benzoyl peroxide has been investigated only in relation to propylamine[127], butylamine[140], and benzylamine[144-146]. The ideas concerning the mechanisms of these reactions have been only slightly elaborated.

When primary or secondary amines interact with *p*-nitrobenzenesulphonyl peroxide with subsequent hydrolysis, carbonyl compounds are obtained, frequently in good yields. Imines are formed in the intermediate oxidation stages and can sometimes be isolated. The process apparently begins with nucleophilic attack by the amine on the peroxide, analogous to reaction (17), and then yet another sulphonic acid molecule is split off from compound (XXXVII):

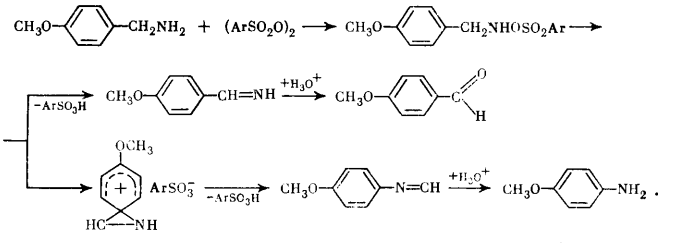


(18)

(XXXVII)

The electrophilic nature of the peroxide and its tendency to split off the $ArSO_3^-$ residue favour this two-electron mechanism.

The "anomalous" course of the reaction has been studied[148]. In the oxidation of, for example, *p*-methoxybenzylamine or diphenylmethylamine the products are *p*-methoxyaniline or benzaldehyde instead of *p*-methoxybenzaldehyde or benzophenone expected on the basis of mechanism (18). These results have been explained by the migration of the aryl residue from the carbon atom to the positively charged nitrogen atom arising on ionisation of a compound of type (XXXVII):



It has been shown[148] that the radical variants of the mechanism are less probable.

The oxidation of amines by dicyclohexyl peroxydicarbonate $(C_6H_{11}OCOO)_2$ has been investigated[141]. In the presence of an excess of the amine, the reactions with triethylamine, *N*-diethylethanolamine, and *N*-ethyldiethanolamine obey a second-order kinetic equation and are accompanied by chemiluminescence. A radical mechanism analogous to mechanism (16) has been proposed.

The oxidation of amines by potassium persulphate in water has been studied[149-156]. According to the characteristics of the rate and the reaction mechanism, the authors divided amines into two groups[149,150]. Primary and secondary amines were assigned to the first group. Their oxidation products have not been determined, but the rate obeys a second-order kinetic equation and is proportional to the KOH concentration. Primary amines are oxidised more slowly than secondary amines. The initial rates of oxidation of amines in this group are proportional to their pK_a, which has been explained by complex formation between the amine and the peroxide in the slow stage. The reaction mechanism has not been established, but it is probably of a non-radical type[149-152].

Tertiary amines and aminoalcohols were assigned to the second group. The oxidation of tertiary amines[149,150,153-156] results in the formation of secondary amines and carbonyl compounds. Diethylvinylamine, which gives rise to diethylamine and acetaldehyde on hydrolysis, was detected among the products of the reaction with triethylamine. The oxidation of tertiary and secondary aminoalcohols[149-150,152,154-166] leads to secondary or primary aminoalcohols and carbonyl compounds respectively. In the case of triethylamine, diethanolamine, and *N*-ethyldiethanolamine, formaldehyde is present among the products, i.e. oxidative fragmentation takes place. The kinetics of the above reactions are fairly complex; fractional reaction orders, the acceleration of the consumption of the oxidant by the reaction products, and the dependence of the rate of oxidation on the presence of radical chain process inhibitors are observed. The rate is not

simply related to the basicity of the amines; the addition of KOH has a different and more complex effect on the rate than for amines in the first group. These data can be accounted for by the involvement of radicals in the reaction, which is consistent with the finding that some of the reactions of this type induce radical polymerisation.

The mechanism of the oxidation of amines of the second group remains obscure. We believe that the proposed mechanisms[150,153,154,156,158,159] are inadequately founded and are unconvincing. They do not explain or only explain poorly the dependence of the rates of the reactions on the concentration of alkali, their orders, etc. and are not detailed.

The oxidation of amines by potassium persulphate is catalysed by variable-valence metals. These reactions with amines and aminoalcohols have been studied[167–173]. The catalytic effect of metal ions increases in the sequence Co^{2+} < Cu^{2+} < Ag^{+}.[170,172] In most cases the rate of oxidation falls with increasing basicity of the amines[167,172], which the authors explained by a decrease of the activity of the metal ions as a result of the increase of the stability of their complexes with the amines. A reaction mechanism involving the formation of a complex comprising the amine, Ag^+ ions, and persulphate, in which the metal ion behaves as an agent transferring an electron from the amine to the persulphate, has been proposed[170,172]. The reaction products were not determined in the above investigations.

The interaction of persulphate with primary amines in the presence of Ag^+ ions is of preparative value[174]. Amines of the type RCH_2NH_2 are converted into aldimines $RCH{=}NCH_2R$, amines of the type $RR'CHNH_2$ give rise to ketones, while the amines R_3CNH_2 are not oxidised. In contrast to the results of Bacon and Stewart[174], Babu et al.[175] isolated hydroxylamine derivatives and oximes as intermediates in the above reaction. In the presence of an excess of the amine (Am), the rate of reaction is proportional to the concentrations of persulphate and Ag^+, the order with respect to the amine falls with increasing Ag^+ concentration, and the reaction is of first order with respect to the amine in the absence of the catalyst. Neutral salts retard the reaction. These data have been explained by the fact that non-catalysed and catalysed reactions take place simultaneously. Ions of opposite sign react in the slow stage of the latter. The overall rate of the process is expressed by the equation

$$\frac{d[S_2O_8^{2-}]}{dt} = k_1[Am][S_2O_8^{2-}] + k_2[Ag^+][S_2O_8^{2-}] \quad .$$

At a high Ag^+ concentration the quantity $k_1[Am]$ becomes much smaller than $k_2[Ag^+]$ and the order of the reaction with respect to the amine becomes zero. The rate constant k_2 is higher the smaller the stability of the complexes of the amines with Ag^+. The catalysed reaction proceeds via the mechanism

$$S_2O_8^{2-} \rightleftarrows 2SO_4^{\cdot-} \quad ,$$

$$2SO_4^{\cdot-} + Ag^+ \xrightarrow[k_M]{\text{slow}} 2SO_4^{2-} + Ag^{3+} \quad ,$$

$$Ag^{3+} + RNH_2 + H_2O \rightarrow RNHOH + Ag^+ \quad , \qquad (19)$$

according to which $w = k_M[SO_4^{\cdot-}]^2[Ag^+]$. Bearing in mind that $[SO_4^{\cdot-}]^2 = K[S_2O_8^{2-}]$ (where K is the equilibrium constant of the reaction $S_2O_8^{2-} \rightleftharpoons 2SO_4^{\cdot-}$), then $w = k_M K[Ag^+][S_2O_8^{2-}]$ and $k_2 = k_M K$. We may note that the last stage in mechanism (19) is not specified in detail and that an analogous mechanism explains the formation of aldimines.

Secondary amines of the type $(RCH_2)_2NH$ react with persulphate and Ag^+ ions to form aldehydes, while those of the type $(RR'CH)_2NH$ give rise to ketones. Primary amines are formed simultaneously. α-Aminoacids give rise to aldehydes while *N*-methylpiperidine and *N*-methylpyridine are not oxidised. These reactions are more complex than the oxidation of primary amines[176].

In contrast to the data presented above, it has been found[177] that di-isopropylamine and the aminoalcohol $HN(CH_2CHOHCH_3)_2$ are oxidised to hydroxylamine derivatives; the mechanism of these reactions has not been established.

Among the reactions of dialkyl peroxides, only the interaction of di-t-butyl peroxide with tri-n-butylamine, di-isopropylamine, and 4-methyl-2-pentylamine has been investigated[178,179]. t-Butyl alcohol and compounds with $-C{=}N-$ bonds are formed almost quantitatively. The rate of reaction is determined by the stage involving the decomposition of the peroxide into radicals, which dehydrogenate the amine. Two variants of the mechanism have been proposed:

$$(CH_3)_3C\dot{O} + R_2CH{-}NHR' \xrightarrow[-(CH_3)_3COH]{} R_2\dot{C}{-}NHR' \xrightarrow{+(CH_3)_3C\dot{O}} \rightarrow (CH_3)_3COH + R_2C{=}NHR'$$

$$(CH_3)_3C\dot{O} + R_2CH{-}NHR' \rightarrow (CH_3)_3CO^- + R_2CH{-}\dot{\overset{+}{N}}R' \xrightarrow[-(CH_3)_3COH]{} R_2\dot{C}{-}\ddot{N}HR' \rightarrow$$

$$\xrightarrow{(CH_3)_3C\dot{O}} R_2C{=}\overset{+}{N}HR' + (CH_3)_3CO^- \rightarrow R_2C{=}NR' + (CH_3)_3COH \quad .$$

The interaction of hydroperoxides with amines has been studied more widely. It has been shown[180] that these reactions lead to satisfactory yields of the alcohols coresponding to the peroxides. Their mechanism has been studied[179] in relation to the reactions of t-butyl hydroperoxide with an excess of 4-methyl-2-pentylamine, di-isopropylamine, tri-n-propylamine, and 2,4,4-trimethyl-2-pentylamine. All these amines form hydrogen-bonded complexes with the hydroperoxide; t-butyl alcohol was detected among the products. The last of the above amines, which does not contain a hydrogen atom in the α-position relative to the amino-group, reacts at a higher temperature than the other amines and gives rise to 2,4,4-trimethyl-2-nitropentane and the products of the thermal decomposition of the hydroperoxide. The reaction mechanism is unknown. The first three amines are converted respectively into the ketimine (XXXVIII), ammonia, and water, into acetone, isopropylamine, water, and the ketimine (XXXIX), and into dipropylamine, propionaldehyde, and its aldol condensation products. Compounds (XL)–(XLIII) are probably formed in addition from tri-n-propylamine.

$(CH_3)_2CHCH_2C{=}NCHCH_2CH(CH_3)_2$ (XXXVIII)

$(CH_3)_2C{=}NCH(CH_3)_2$ (XXXIX)

$C_3H_7NHCHCH_2CH_3$ (XL)
OC_4H_9

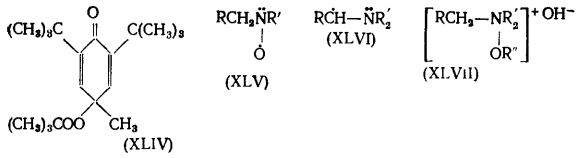
$(C_2H_7)_2NCHCH_2CH_3$ (XLI)
OC_1H_9

$C_3H_7NHCHCH_2CH_3$ (XLII)
$C_3H_7NHCHCH_2CH_3$

$(C_3H_7)_2NCHCH_2CH_3$ (XLIII)
$(C_3H_7)_2NCHCH_2CH_3$

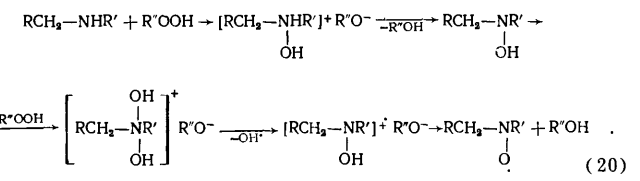
One may therefore assume that the first three amines give rise to dealkylation products and carbonyl compounds, which can be converted into imines by reacting with the initial amine or the amine formed in the reaction. The products (XL)–(XLIII) probably arise from intermediate radicals. The involvement of radicals is confirmed by the retardation of the reactions by radical chain process inhibitors, for example ionol. The formation of the radicals $(CH_3)_3C\dot{O}$ has been demonstrated by the isolation of compound (XLIV)—the product of their interaction with radicals corresponding to

ionol.



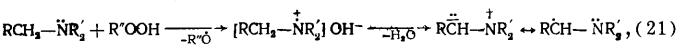
(XLIV) (XLV) (XLVI) (XLVII)

De La Mare[179] explained the set of results obtained in terms of a radical-chain mechanism. The radicals (XLV) or (XLVI) arise in the initiation stage. The formation of the radicals (XLV) in the oxidation of tertiary and secondary amines by t-butyl hydroperoxide has been demonstrated by EPR.[181] The mechanism of their formation is obscure in the case of tertiary amines and that in the reaction with secondary and primary amines is



(20)

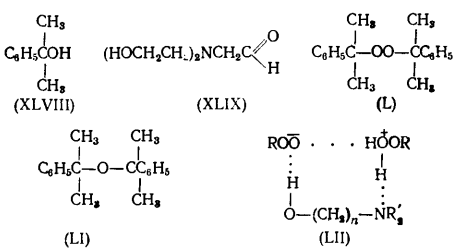
The radicals (XLVI) are obtained via the mechanism



(21)

possibly with the intermediate involvement of the quaternary ammonium salt (XLVII). The chain propagation and termination mechanisms proposed by De La Mare[179] easily explain the mechanisms of the formation of all the reaction products.

The interaction of amines with cumenyl hydroperoxides in water has been studied[182–185]. Two parallel reactions take place with triethanolamine. The rate of one of them is proportional to the concentrations of the amine and the hydroperoxide. The rate of the second reaction is proportional to the square of the concentration of the hydroperoxide and depends on the dielectric constant and the presence of neutral salts. The reaction products—the alcohol (XLVIII), the aldehyde (XLIX), the peroxide (L), oxygen, and possibly the ether (LI)—are believed to be formed on decomposition of complexes of the amine with the hydroperoxide or its dimer. The latter complex is formed only by aminoalcohols, which has been explained by the structure (LII).

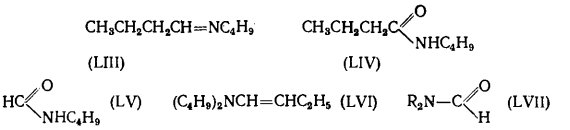


(XLVIII) (XLIX) (L) (LI) (LII)

The mechanism of the decomposition of the complexes is unknown.

Metal compounds catalyse the oxidation of amines by hydroperoxides. Tertiary amines and aminoalcohols are converted into *N*-oxides in high yields, piperidine is converted into 2-piperidinone, and primary amines are converted into oximes. Vanadium, molybdenum, titanium, and tungsten compounds are particularly active. The reaction mechanism has not been established[186]. A study has been made of the kinetics of the reactions of triethylamine and morpholine with cumenyl hydroperoxide catalysed by metal ions[187].

The oxidation of amines by hydrogen peroxide has been little investigated. Only isolated data are available concerning its kinetics and mechanism. Thus it has been shown[188] that in acetonitrile the intermediate in the oxidation of n-butylamine is the aldimine (LIII), which is converted by the peroxide into the amides (LIV) and (LV).



(LIII) (LIV) (LV) (LVI) (LVII)

In addition the corresponding hydroxylamine and oxime are formed. The reaction with di-n-butylamine leads to dibutylhydroxylamine, the aldimine (LIII), and its oxidation products. Tri-n-butylamine gives rise to an amine oxide and the enamine (LVI), which hydrolyses to dibutylamine and butyraldehyde. It has been established[189] that the hydroxylamines formed in the oxidation of secondary amines on treatment with an aqueous H_2O_2 solution always contain an admixture of the corresponding *N*-formyldialkylamines (LVII) and a mechanism of their formation has been proposed. The kinetics of the oxidation of triethylamine by hydrogen peroxide have been investigated[190].

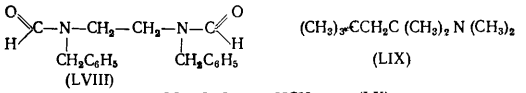
The characteristics of the catalytic oxidation of amines by hydrogen peroxide in the presence of $NaWO_4$ or $NaMoO_4$ have been studied[191,192]. The rate of reaction is proportional to the concentrations of the amine and the catalyst, decreasing on passing from tertiary to secondary amines and with increasing branching of the hydrocarbon residues at the nitrogen atom. It has been suggested that the primary products are amine oxides or amine oxide hydrates. Those obtained from ammonia and primary and secondary amines isomerise to hydroxylamines, which have been identified. Among other products, oximes and in certain cases carbonyl compounds have been detected. The formation of oxides from tertiary amines and of *N*,*N*-dialkylhydroxylamines from secondary amines on treatment with hydrogen peroxide in the presence of $NaWO_4$ has also been established in another study[193]. t-Butylamine is converted into a nitro-compound, while amines in which a primary or secondary carbon atom are linked to the NH_2 group give rise to aldoximes or ketoximes (isomerisation products of nitroso-compounds). It is believed that the above reactions involve electrophilic substitution at the nitrogen atom.

It is noteworthy that, despite the incompleteness of the data presented, one can postulate that radicals are involved in the reactions. It may be that radical processes take place simultaneously with electrophilic substitution. This is indicated by the formation of imines, enamines, and carbonyl compounds, usually obtained in the radical oxidation reactions of amines. One cannot rule out the possibility that radical reactions involving oxidation by hydrogen peroxide begin with reactions of types (20) and (21).

10. Other Oxidation Reactions

The oxidation of tri-n-alkylamines with $N-CH_2-CH_2$ residues by a suspension of hydrated manganese dioxide ($HOMnO_x$) in cyclohexane[114,195] leads to the formation of dialkylformamides. The hydrolysis of the reaction mixture gives rise also to dialkylamines. It has been suggested that the "$HOMnO_x$" surface generates HȮ radicals, which oxidise the adsorbed amines to carbinolamines. As in the reaction of amines with ozone, the latter hydrolyse to dialkylamines or are dehydrated to enamines, whose oxidation gives rise to dialkylformamides.

The formation of carbinolamines and their reactions account for the nature of the products of the reactions of various tertiary amines with "$HOMnO_x$". Thus benzaldehyde has been obtained from benzyldimethyl-, benzyldiethyl-, and tribenzyl-amines. 1,4-Dibenzylpiperazine gives rise to compound (LVIII). Cyclohexyldimethyl- and cyclohexyldiethylamines are converted into cyclohexanone, while the latter amines also give rise to acetaldehyde. Triethylenediamine and 1,2-dipiperidinoethane are converted into 1,4-diformylpiperazine and 1-formylpiperidine respectively. The amine (LIX) is converted into compound (LX).[195,196]



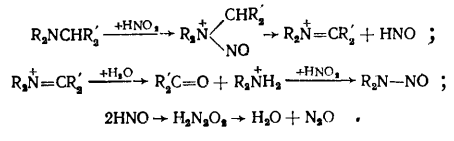
(LVIII)

$(CH_3)_3CCH_2C(CH_3)_2N(CH_3)_2$ (LIX)

$(CH_3)_3CCH_2C(CH_3)_2NHCH_3$ (LX)

Nitrous acid in aqueous acetic acid reacts with tertiary amines via the mechanism $R_2NCHR'_2 + HNO_2 \rightarrow R_2N{-}NO + R'_2C{=}O$.

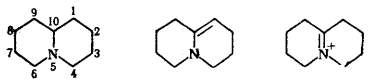
Nitrous oxide is present among the products. The introduction of substituents in the *meta*- or *para*-positions in one of the tribenzylamine rings influences the process: the fractions of unsubstituted benzaldehyde and substituted nitrosamine are given by the Hammett equation with a small negative value of ρ. The rate of reaction decreases with decrease of the basicity of the amines. Quinuclidine does not react. Substituents in one of the α-positions of tribenzylamine or benzyldiethylamine lead to the preferential formation of benzaldehyde or acetaldehyde regardless of the nature of the substituents. The amine $C_6H_5CD_2N(CH_2C_6H_5)_2$ is converted into deuterated and non-deuterated benzaldehyde in proportions of 1 : 8 ($k_H/k_D = 3.78$). The results have been explained by a heterolytic mechanism[197,198]:



It has been suggested that the elimination of HNO takes place intramolecularly in the reaction with a cyclic transition state. The mechanism involving the intermediate formation of ammonium radical-cations and nitric oxide as one of the reaction products[199] does not explain the formation of nitrous oxide, while the nucleophilic dealkylation mechanism[200] is inconsistent with the isotope effect. Nor can one rule out a mechanism in which NO^+ abstracts a hydride ion from the α-carbon atom of the amine[198].

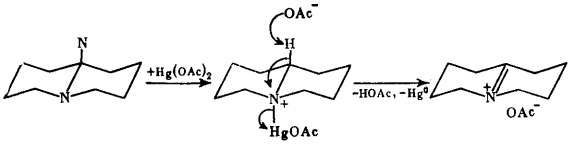
In the oxidation of triethylamine by iron(III) complexes of phenanthroline derivatives or the molybdenum(V) octacyanide complex[80] an electron is transferred from the amine to the oxidant with formation of ammonium radical-cations.

The oxidation of cyclic tertiary amines by mercury(II) acetate has been investigated[92,201-205]. The reaction leads to the formation of enamines. For example, the enamine (LXII) is formed from quinolizidine (LXI) and is converted into a salt.



(LXI) (LXII) (LXIII)

The oxidation apparently proceeds via a heterocyclic mechanism involving structure (LXIII):



$Hg(OAc)_2 + Hg^0 \rightarrow Hg_2(OAc)_2$.

Quinolizidine-10-*d* is oxidised 2.3 times more slowly, so that the rate is limited by the decomposition and not the formation of the complex illustrated in the scheme above. The C–H bond involving the eliminated proton must be located in the *trans*-position relative to the N–Hg bond. A one-electron reaction mechanism is also not ruled out.

The data described above show that most of the reactions considered have radical or radical chain mechanisms. However, in only a few instances has direct evidence been obtained for the involvement of the radicals and their decisive role in the formation of the main reaction products established. We include in evidence of this type the observation of chemically induced nuclear polarisation in the products, the observation of EPR and optical spectra of the radicals or radical-cations involved in the formation of the products, the observation of the chemiluminescence of the reaction mixture and the initiation of polymerisation processes by the reaction mixture, and the presence of an induction period, which depends on the presence of inhibitors or initiators of radical chain reactions. Such evidence has been obtained for the oxidation of amines by diazonium and iodonium salts, ClO_2, quinonoid and peroxide compounds, etc., but in such cases there is no certainty that the main reaction products are obtained solely via the radical mechanism.

In other instances the radical mechanism has been justified indirectly. The relevant evidence has been obtained by considering kinetic data (in particular, the nature of the dependence of the rate of oxidation on the substituents in the substrate and the oxidant), the nature of the products formed, etc. Such combined indirect evidence constitutes a serious argument in support of the proposed mechanisms but cannot be regarded as their unambiguous confirmation.

The radical mechanisms examined can be classified in terms of the mode of generation and the nature of the radicals formed in the key stages. In most reactions the key role is due to the ammonium radical-cations, but direct evidence for their involvement in the reactions is available in only rare instances. These radicals can be obtained on electron transfer from the amines to the oxidants. If the transfer is reversible and limits the rate of oxidation, then the rates of reaction of a specified amine with a series of oxidants are correlated with their oxidation potentials E^0 and the rates of oxidation of different amines are correlated with the E^0 and the sum of the σ^* constants of the substituents at the nitrogen atom of the amine or with the E^0 and the photoionisation potentials of the amines[82]. The validity of these correlations may serve as a criterion of reversible electron transfer from the amine to the oxidant in the slow stage of the reaction. (Its other features were frequently discussed above.)

Yet another way of forming ammonium radical-cations consists in the decomposition of an intermediate compound or complex of the amine with the oxidant. The choice between this pathway and electron transfer is important for the understanding of the mechanism; however, frequently, such choice is based on indirect data in view of the lack of detailed information about the reaction kinetics. In only relatively

rare instances (see Section III, 2) has it been shown clearly that there is no direct electron transfer in the slow stage of the reaction.

In certain reactions (see, for example, Sections III, 4 and III, 6) the primary formation of α-amino radicals or the competitive formation of these radicals and ammonium radical-cations has been postulated. The rates of such reactions do not obey the above correlations. However, one should note that the involvement of α-amine radicals in the reactions, which can be regarded as likely on the basis of the available experimental data, has not been demonstrated directly. The observation of the primary isotope effect of deuterium cannot be regarded as direct evidence, since it can arise in the transfer of protons or hydride ions in the slow stage.

The formation of nitroxy-radicals has been established in the interaction of amines with t-butyl hydroperoxide. It is natural to postulate their key role in radical reactions of hydroperoxides and possibly of hydrogen peroxide with amines, particularly in those cases where compounds with nitrogen–oxygen bonds are formed.

As can be seen from the data presented above, the non-radical (molecular and ionic) amine oxidation mechanisms have been specified in less detail and are less well founded than the radical mechanisms. This applies particularly to mechanisms where the shift of a hydride ion is postulated. We may note that doubts have arisen in recent years as to whether the hydride ion shift is an elementary step and not consecutive transfer of an electron and a hydrogen atom or of two electrons and a proton[24,37].

We emphasise the importance of the results obtained in the study of the mechanism of the oxidation of amines with the aid of CIDNP. This method not only permits an unambiguous solution of the problem of the involvement of radicals in the formation of the reaction products but also allows one to derive information about the fine details of the mechanism, in particular to identify the radical pairs whose radicals are converted into the products (see Section III, 2 and Section III, 4).

In conclusion we may note that, despite the considerable advances in the study of individual amine oxidation reactions, this field has still not been adequately studied.

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The Molecular Geometry of Nitro-compounds

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A systematic account is given of data on the molecular geometries of approximately 300 nitro-compounds obtained for the vapours by gas electron diffraction and microwave spectroscopy and for the crystalline phases by X-ray diffraction. Certain rules have been formulated for the variation of the geometrical parameters of the molecules in the principal classes of nitro-compounds: inorganic, aliphatic, alicyclic, and aromatic nitro-compounds, nitroamines, and salts and complexes of nitro-alkanes and aromatic nitro-compounds.
The bibliography includes 181 references.

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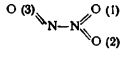
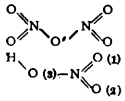
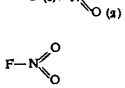
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I. INTRODUCTION

Nitro-compounds constitute a class of compounds which is important for practical and theoretical chemistry. The nitrogen atom in the NO_2 group has a specific valence state. From the standpoint of the classical theory of chemical structures, the valence of the nitrogen atom in the nitro-group $-N\begin{matrix}=O\\ \\ =O\end{matrix}$ is five, but approximate quantum-chemical ideas do not allow an increase of the valence of the nitrogen atom above four. On the basis of the concept that the nitrogen atom is quadrivalent, pronounced electron-accepting properties of the nitro-group have been postulated.

Analysis of data on the geometrical structure of the molecules is particularly important for the determination of the relation between the chemical structure and physicochemical properties of nitro-compounds. Numerous studies on these compounds have now been made by different methods: by gas electron diffraction (GE) and microwave spectroscopy (MW) for the vapours of the substances and by X-ray diffraction (XD) and neutron diffraction (to a much lesser extent) for the crystalline phase. Unfortunately, the results are not uniformly distributed with respect to different classes of compounds. The majority of data refer to the structures of aromatic nitro-compounds in the crystalline phase; there have been few electron diffraction and microwave studies on the free molecules in the gas phase.

Table 1. Geometrical parameters of inorganic nitro-compounds in the gas phase.

Structural formula	Symmetry	Parameters of nitro-group			Other bonds and valence angles	Method	Parameter	References
		r(N=O), Å	∠ONO, deg	r(O...O), Å				
	C_{2v}	1.1934(10) 1.202(3)	134.07(1.0) 134.0(1.3)	2.198 2.213	—	MW GE	r_a r_a	[1] [2]
	C_s	NO(1) 1.202(6) NO(2) 1.217(7)	129.8(1.1)	2.190	r(NO(3))=1.142(4) Å r(NN)=1.864(7) Å ∠O(3)NN=105.1(0.1)° ∠NNO(1)=112.7(0.7)° ∠NNO(2)=117.5(0.4)°	MW	r_s	[4]
	D_{2h}	1.190(2)	135.4(0.6)	2.201	r(NN)=1.782(8) Å	GE	r_a	[5]
	—	1.21(1)	134(5)		r(NO′)=1.46(2) Å, ∠NO′N95(30)°	GE		[6]
	C_s	NO(1) 1.211(5) NO(2) 1.199(5)	130.2(0.5)	2.184	r(NO(3))=1.406(5) Å r(OH)=0.964(10) Å ∠O(1)NO(3)=115.9(0.5)° ∠O(2)NO(3)=113.9(0.5)°	MW	r_s	[7]
	C_{2v}	1.180(5)	136.0(1.5)	2.188	r(NF)=1.467(15) Å	MW	r_s	[8]
	C_{2v}	1.202(20)	130.6(2.0)	2.181	r(NCl)=1.840(20) Å	MW	r_0	[9]
	C_s	1.206	130.1(0.5)	2.185	r(NN)=1.427 (3) Å r(NH)=1.005(15) Å ∠HNH=115.2(3.0)° ∠Φ=51.8(1.5)°	MW	r_0	[10]

Note. The errors of the determination of the parameters, referring to the last significant figures, are given in brackets, for example 1.190(2) Å = 1.190 ± 0.002 Å and 130.2(0.5)° = 130.2 ± 0.5°. For the differences between the types of the parameters r_a, r_0, and r_s due to vibrational effects and usually amounting to <0.01 Å, see, for example, Vilkov et al.[3] The bond length r(N=O) = 1.206 Å in NH_2NO_2 was fixed and was not varied in refining the parameters; Φ is the angle between the NH_2 and NNO_2 planes.

The task of the analysis of the molecular structure consisted in the determination of the rules governing the variation of the geometries of the groups CNO_2 (*C*-nitro-compounds), NNO_2 (*N*-nitroamines), and ONO_2 (*O*-nitro-compounds) as a function of the class of compound and the nature of the atoms and groups of atoms linked to the above groups. On the other hand, it is necessary to elucidate the influence of the NO_2 group on the neighbouring groups of atoms in the molecules of nitro-compounds. The molecular confirmation and the nature of the internal rotation of the nitro-group are important.

The review includes literature data up to 1978 inclusive and the results of a few studies in 1979. Since virtually all the data for the crystal structures published up to 1971 have been included in handbooks, references to the latter are given.

II. GEOMETRICAL STRUCTURE OF THE MOLECULES OF NITRO-COMPOUNDS IN THE GAS PHASE

1. Inorganic Nitro-Compounds

The determination of gas-phase structural data for inorganic nitro-compounds such as nitrogen oxides, nitric acid, and nitryl halides is associated with considerable experimental difficulties. As apparatus and experimental techniques have improved, the molecular geometries of these compounds have been reinvestigated. The results of the latest electron diffraction and microwave studies are presented in Table 1.

The N=O bond length in the nitro-group is almost constant and amounts to 1.20 Å on average. The ONO valence angle varies within wide limits, from 130° to 136°. The smallest value of r(N=O) and the greatest value of ∠ONO have been found for the NO_2F molecule, which is attributed to the high electronegativity of the fluorine atom[8]. We may note that, despite certain differences in the N=O bond lengths and ONO valence angles, the distance between the oxygen atoms in the nitro-group remains constant to within 0.02 Å.

The N_2O_3 and N_2O_4 molecules are characterised by unusually low N–N bonds, whose length exceeds by 0.3 Å the lengths of the corresponding bonds in hydrazine and its derivatives[3]. The nature of the N–N bond in these molecules has been discussed, for example, in a review[11]. The N–F and N–Cl bond lengths in the NO_2F and NO_2Cl molecules are greater than these bond lengths in NF_3 (1.36 Å) and NCl_3 (1.77 Å).

The molecules of the compounds presented in Table 1 are planar with the exception of N_2O_5 and NH_2NO_2. The conformation of the N_2O_5 molecule has not been reliably determined owing to the rotational movement of the nitro-group. In nitramide the amino-nitrogen atom has a pyramidal configuration of the bonds. In the determination of the geometry of this compound from the microwave spectrum[10], the N=O bond length, which is an important parameter, was assumed†. It has been shown[12] that another set of parameters, in which r(N=O) = 1.232 Å and r(N–N) = 1.381 Å, is consistent with the moments of inertia obtained[10]; this is consistent with the corresponding parameters of nitroamines (see Table 4 below).

2. Organic Nitro-Compounds

The majority of the molecular structures of simple aliphatic and aromatic nitro-compounds as well as nitroamines were investigated in the gas phase for the first time in the course of the last decade. The earlier data for the molecular geometries of CH_3NO_2, CH_3ONO_2, and $C(NO_2)_4$ have also been

Table 2. Principal geometrical parameters of the molecules of aliphatic nitro-compounds in the gas phase (X = C, F, Cl, or Br).

Compound	r (N=O), Å	r (C–N), Å	r (C–X), Å	∠ONO, deg	∠XCN, deg	Conformation	Method	Parameter	Refs.
CH_3NO_2	1.224 (5)	1.489 (5)	—	125.3(0.5)	—	free rot.	MW	r_a	[13]
CH_2ClNO_2	1.228 (2)	1.506 (9)	1.765 (9)	129.0 (1.5)	114.0 (1.0)	hindered rot.	GE	r_a	[14, 15]
CF_3NO_2	[1.22]	1.490	[1.325]	[127]	[109]	free rot.	MW	r_0	[16]
CF_3NO_2	1.21 (1)	1.56 (2)	1.325 (5)	132 (2)	109 (1)	hindered rot.	GE	r_a	[17]
CCl_3NO_2	1.190 (6)	1.594 (20)	1.726 (5)	131.7 (2.6)	106.0 (1.1)	hindered rot.	GE	r_a	[18]
CBr_3NO_2	1.22 (1)	1.59 (2)	1.92 (1)	134 (3)	208.3 (2.5)	hindered rot.	GE	r_a	[17]
$C_2H_5NO_2$	1.213 (3)	1.505 (3)	[1.540]	[134]	—	C_s	MW	r_0	[19]
$CH_2{=}CHNO_2$	1.220 (6), 1.234 (4)	1.471 (3)	1.322 (5)	126.0 (0.3)	121.2 (0.2)	C_s, planar	MW	r_s	[20]
▷—NO_2	1.213 (21)	1.488 (20)	[1.511]	[130]	—	C_s, bisector type	MW	r_0	[21]
$CCl_2(NO_2)_2$	1.224 (4)	1.506 (12)	1.757 (8)	124.9 (1.1)	109.7 (0.7)	C_2; φ=74(3)°	GE	r_a	[22]
$CH(NO_2)_3$	1.219 (3)	1.505 (5)	—	128.6 (1.0)	—	C_3; φ=26(1)°	GE	r_a	[23]
$CCl(NO_2)_3$	1.213 (3)	1.513 (3)	1.712 (4)	128.3 (0.6)	112.1 (0.5)	C_3; φ=49(1)°	GE	r_a	[23]
$CBr(NO_2)_3$	1.214 (3)	1.514 (6)	1.885 (9)	132.5 (2.0)	111.3 (1.0)	C_3; φ=49(1)°	GE	r_a	[23]
$C(NO_2)_4$	1.218 (2)	1.526 (6)	—	129.3 (1.0)	—	S_4; φ=47(4)°	GE	r_a	[24]

Note. The assumed values of the parameters are given in square brackets; φ is the angle of rotation of the NO_2 group about the C–N bond; φ = 0° for the coplanar disposition of the nitro-groups in $CCl_2(NO_2)_2$ and $C(NO_2)_4$ (D_{2d}) and for the planar arrangement of the XCNO atoms in $CX(NO_2)_3$.

† Here and henceforth the term "assumed" implies that the parameter was fixed and was not varied in the minimisation process whereby the parameters were refined.

revised. The principal structural parameters are presented in Table 2. A fairly detailed discussion of the molecular structures of organic nitro-compounds in the gas phase can be found in a book[3] and in a review[25]. We shall therefore confine ourselves to only a brief consideration of the principal characteristics of their geometrical structures.

The study of the molecular structures of aliphatic nitro-compounds (Table 2) has shown that the parameters of the nitro-group depend little on the substituent. In particular, the mutual influence of several nitro-groups in polynitroalkanes is weakly reflected in the geometry of these groups. The constancy of the N=O bond length (the average value is 1.22 Å) is particularly characteristic. The ONO angle is on average 129° with a maximum deviation of ±4° (we may note that angles exceeding 130° are quoted with large errors). The minimum value ∠ONO = 125° has been found for nitromethane and dichlorodinitromethane.

The C–N bond lengths in nitroalkanes are in the range 1.49–1.53 Å. Halogenopicrins, whose structure is discussed below, are an exception. There is a tendency towards an increase of r(C–N) with increase of the number of nitro-groups:

Compound	CH_3NO_2	$CH(NO_2)_3$	$C(NO_2)_4$
r(C–N), Å	1.489 (5)	1.505 (5)	1.526 (6) . #

A characteristic geometrical feature of the CNO_2 group is its planar structure[13,16,19,20].

Under the influence of nitro-groups, the lengths of the C–Cl and C–Br bonds adjoining them diminish, which is particularly notable in trinitro-compounds. The bond lengths r(C–Cl) = 1.712(4) Å in $CCl(NO_2)_3$ and r(C–Br) = 1.885(9) Å in $CBr(NO_2)_3$ are the shortest for bonds of the type $\geq$C–X (X = Cl or Br) and are virtually identical with the corresponding bond lengths in the vinyl derivatives.

Halogenopicrins CX_3NO_2 (X = F, Cl, or Br), the electron diffraction data for which conflict with the results of microwave studies on CH_3NO_2 [13,27] and CF_3NO_2,[16] occupy a special place among the mononitroalkanes presented in Table 2. Electron diffraction study of halogenopicrin molecules yielded unusually high C–N bond lengths (up to 1.59 Å), demonstrated hindered rotation about this bond with a barrier of approximately 3 kcal mol^{-1}, and revealed a slight deviation from the planar structure of the CNO_2 groups, leading to a preferred staggered conformation. According to microwave data for CF_3NO_2 (and also CH_3NO_2), the C–N bond length is 1.49 Å, the rotation about this bond is free, and the CNO_2 group is planar. Analysis of electron diffraction data, carried out by the compilers of a handbook[28], led them to the conclusion that these had been obtained with a lower accuracy than indicated by the authors[17,18] [for example, the real error of the determination of r(C–N) is 0.06 Å] and that the barrier to rotation is probably too high. Thus the problem of the molecular structure of halogenopicrins cannot be regarded as ultimately solved.

The molecules of nitroethane, nitroethylene, and nitrocyclopropane have the C_S symmetry. The NO_2 group in nitroethane is in the same plane as the C–N and C–C bonds, and the four hydrogen atoms are arranged symmetrically above and below this plane. The nitroethylene molecule is also planar. Only a bisectorial conformer has been found for nitrocyclopropane in which the plane of the nitro-group is at right angles to the plane of the three-membered ring. The barrier to rotation about the C–N bond in the nitrocyclopropane molecule has been estimated as 1100 ± 500 cm^{-1} or 3.3 ± 1.5 kcal mol^{-1}.

A characteristic feature of the conformation of polynitroalkane molecules in the gas phase is that the angles of rotation of the nitro-groups relative to the N–C–X plane (X = H, Cl, Br, or N) differ from 0° (Table 2). The non-bonded O...Hal and N...O distances are reduced compared with the sum of the van der Waals radii, while the O...O distances are normal. Theoretical calculations of the molecular conformations of trinitro-compounds[29] and tetranitromethane[30] on the basis of a mechanical model agree satisfactorily with experiment; such agreement has not been obtained for dichlorodinitromethane[29].

The geometrical parameters of aromatic nitro-compounds are presented in Table 3. Comparison of the C–N bond lengths and ONO angles in aromatic and aliphatic nitro-compounds shows that as a rule both these parameters are smaller for benzene derivatives than for saturated aliphatic compounds. On the other hand, the equality of the r(C–N) in aliphatic and aromatic nitro-compounds has been noted in a number of monographs (see, for example, Feuer[36]) on the basis of old experimental data, which is difficult to reconcile with the ideas concerning their electronic structure.

The principal conclusion which follows from the study of the molecular structures of aromatic nitro-compounds in the gas phase is that the geometry of their benzene ring is altered. Thus the average C...C bond length§ in $C_6H_5NO_2$, *sym*-$C_6H_3(NO)_3$, *p*-$C_6H_4(NO_2)_2$, and *p*-$ClC_6H_4NO_2$ is smaller than in benzene [r_g = 1.399(1) Å] [3] and is almost independent of the number of nitro-groups. The $CC_{NO_2}C$ valence angle at the carbon atom linked to the nitro-group is greater than 120° in all the compounds listed in Table 3 except *o*-$C_6H_4(NO_2)_2$.

It has been shown in relation to *p*-nitroaniline and *p*-chloronitrobenzene that the nitro-group shortens the C–X (X = Cl or NH_2) bonds, while the CC_XC valence angle hardly changes:

Compound	$C_6H_5NH_2$ [3]	$NH_2C_6H_4NO_2$ [35]	C_6H_5Cl [37]	$ClC_6H_4NO_2$ [34]
r(C–X), Å	1,402 (2)	1,367 (17)	1,737 (5)	1,707 (4)
$\angle CC_XC$, deg	119,5 (2)	119,8 (1,7)	121,7 (0.6)	120,5 (0,6)

Note. The numbers in square brackets denote references (Ed. of Translation).

The *o*-dinitrobenzene molecule, in which there is appreciable steric hindrance, is non-planar and its conformation is characterised not only by the rotation of the nitro-group but also by the deviation of the C–N bonds by 3.6° from the direction of the bisector and by their displacement from the plane of the ring (by approximately 1°) (which fully agrees with a conformational calculation[38]). The non-planar conformations of the other compounds in Table 3, determined by electron diffraction, is associated with the torsional vibrations of the nitro-groups. Allowance for these vibrations leads to a planar equilibrium model with a barrier to rotation $V_2 \cong 5$ kcal mol^{-1}.[39]

In analysing the structural data for *N*-nitroamines (Table 4), it is important to elucidate the dependence of the change in the N–N bond length and in the molecular configuration on

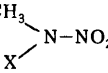
The value r(C–N) = 1.47 Å was quoted in an early electron diffraction study[26]. The difference of 0.05 Å from the result of a reinvestigation[24] presented here can be associated with the inaccuracy of the earlier visual method.

§ The bond lengths in the benzene rings of the molecules investigated were not found to be unequal, although models with different bond lengths have been considered in structural analysis.

Table 3. Principal geometrical parameters of aromatic nitro-compounds in the gas phase.

Compound	r(N=O), Å	r(C–N), Å	r(C...C), Å	∠ONO, deg	∠$CCNO_2$C, deg	φ_{NO_2}, deg	References
$C_6H_5NO_2$	1.226	1.492	1.391	124.4	125.0	0	[31, 32]
o-$C_6H_4(NO_2)_2$	1.224 (2)	1.475 (12)	1.397 (2)	124.9 (0.5)	120.4 (1.2)	31.1 (1.8)	[33]
p-$C_6H_4(NO_2)_2$	1.221 (2)	1.463 (10)	1.392 (2)	125.8 (0.5)	122.9 (0.9)	18.5 (4.1)	[33]
sym-$C_6H_3(NO_2)_3$	1.224 (2)	1.475 (5)	1.388 (2)	125.7 (0.5)	123.2 (0.9)	21.0 (2.3)	[33]
p-$ClC_6H_4NO_2$	1.237 (3)	1.469 (13)	1.388 (1)	123.0 (0.9)	122.6 (1.1)	18.9 (5.3)	[34]
p-$H_2NC_6H_4NO_2$	1.225 (2)	1.470 (11)	1.402 (3)	124.7 (0.7)	122.8 (1.4)	17.4 (7.4)	[35]

Note. Nitrobenzene was investigated by microwave spectroscopy (parameters r_S); the remaining compounds were studied by electron diffraction (parameters r_g); ϕ is the angle of rotation of the NO_2 group about the C–N bond.

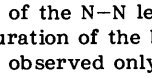
Table 4. Principal parameters of the molecules of *N*-methylnitroamines having the general formula  in the gas phase.

X	r(N=O), Å	r(N–N), Å	r(C–N), Å	∠ONO*	∠CNN*	∠CNX*	∠CNNO*	References
H	1.228 (3)	1.381 (6)	1.452 (6)	125.3 (1.0)	109.0 (1.3)	119 (1)	28	[12]
CH_3	1.223 (2)	1.382 (3)	1.460 (3)	130.4 (1.5)	116.2 (0.3)	127.6 (0.6)	0	[40]
CH_2Cl*	1.220 (3)	1.426 (10) ***		123.5 (0.5)	116.2 (0.5)	127.5 (0.5)	35	[41]
Cl**	1.209 (2)	1.469 (5)	1.478 (5)	128.5 (0.9)	112.9 (1.5)	115.0 (1.2)	27	[12]
NO_2	1.231 (3)	1.480 (5)	1.494 (6)	132 (1)	107.5 (1.1)	107.5 (1.1)	28	[42]

*r(C–Cl) = 1.790(7) Å, ∠NCCl = 112.3(0.8)°.
**r(N–Cl) = 1.720(4) Å, ∠ClNN = 108.4(1.3)°; the dihedral ClNNO angle is 24.4°.
***The average value is quoted.

the substituents at the amino-nitrogen atom. It was found that the replacement of the CH_3 group or a hydrogen atom in methylamines by a chlorine atom or the NO_2 group leads to a marked increase of the N–N length (by approximately 0.1 Å). A planar configuration of the bonds involving the amino-nitrogen atom is observed only in the $(CH_3)_2NNO_2$ and $(CH_2Cl)CH_3NNO_2$ molecules. Moreover, whereas the dimethylnitramine molecule is planar overall†, the nitro-group in the *N*-chloromethyl-*N*-methylnitroamine molecule has been rotated by 35°. In other *N*-substituted nitroamines and nitramide (Table 1) the amino-nitrogen atom has a pyramidal configuration of the bonds. This leads to the conclusion that the configuration of the amino-nitrogen bonds depends only on the atoms and groups of atoms linked directly to the nitrogen atom. Overall, greater differences between the structural parameters are observed for *N*-nitroamines than for *C*-nitro-compounds. The complex geometrical relations for nitroamines require further study.

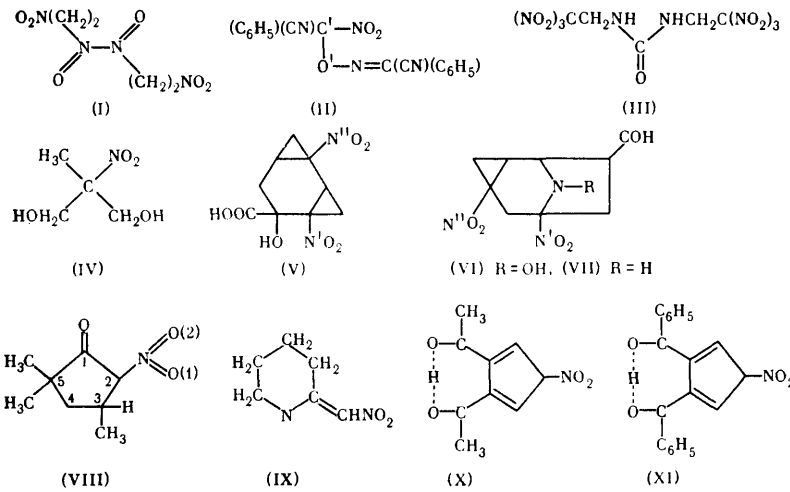
† Here and henceforth the term "assumed" implies that the parameter was fixed and was not varied in the minimisation process whereby the parameters were refined.

The molecular structures of *O*-nitro-compounds have been hardly investigated in the gas phase. Fairly reliable structural data have been obtained only for methyl nitrate[43]. The  molecule has the C_s symmetry and a planar skeleton with the following parameters: r(N–O) = 1.205(5) Å, r(N–O′) = 1.402(5) Å, r(C–O′) = 1.437(5) Å, ∠O′NO = 118.1(0.3)° (*cis*), ∠O′NO = 112.4(0.3)° (*trans*), and ∠CO′N = 112.7(0.3)°. Thus the parameters of the nitro-group are close to the corresponding parameters of aliphatic nitro-compounds and nitroamines.

III. THE GEOMETRICAL STRUCTURE OF THE MOLECULES OF NITRO-COMPOUNDS IN THE CRYSTAL

1. Aliphatic and Alicyclic *C*-Nitro-compounds

There have been only a few studies of aliphatic and alicyclic nitro-compounds by X-ray diffraction and their accuracy has been low in a number of instances. The structures whose parameters have been obtained with satisfactory accuracy, are presented in Table 5.



Owing to the scatter of the bond lengths and valence angles, it is difficult to compare them with the analogous compounds in the gas phase. Averaging of the geometrical parameters of the CNO_2 groups yields the following values: $r(N=O)$ = 1.21 Å, $r(C-N)$ = 1.50 Å, and ∠ONO = 124°. The average N=O and C–N internuclear distances obtained agree, within the limits of the errors, with the average values of the same distances in the compounds investigated in the gas phase; the ONO angle is somewhat smaller.

Table 5. Geometrical parameters of the CNO_2 group in a series of aliphatic and alicyclic nitro-compounds in the crystalline phase.

Compound	r(N=O), Å	r(C–N), Å	∠ONO,*	∠NCC,*	Refs.
(I)	1.205(5) * 1.198(4)	1.485 (5)*	123.2 (0.4)	112.3 (0.4)	[44]
(II)	1.165(7) 1.126(6)	1.617 (6)	130.0 (0.5)	107.9 (0.3)	[45]
(III)	1.210(15)	1.510 (15)	127.2 (1.1)	111.8—113.3**	[46]
(IV)	1.210(4) 1.200(4)	1.506 (4)	122.3 (0.3)	105.6—108.9	[47]
(V)	$N'O_2$ 1.232(4); 1.217(4) $N''O_2$ 1.224(4)	1.486 (4) 1.476 (4)	122.7 (0.3) 123.4 (0.3)	112.6—113.3 113.4—115.4	[48]
(VI), (VII)***	$N'O_2$ 1.209(4) $N''O_2$ 1.219(5)	1.528 (3) 1.482 (3)	124.0 (0.2) 122.8 (0.2)	108.0—110.8 114.1—115.7	[49]
(VIII)	1.222(5) 1.197(5)	1.486 (4)	123.7 (0.3)	109.5 (0.2) 114.0 (0.2)	[50]
(IX)	1.246(7) 1.262(7)	1.362 (8)	117.7 (0.6)	126.0 (0.7)	[51]
(X)	1.226(3)	1.432 (3)	122.9 (0.2)	124.4 (0.2)	[52]
(XI)	1.230(2)	1.433 (4)	123.6 (0.2)	124.5 (0.2)	[52]

Note. The values of $r(N=O)$ in the NO_2 group are given as independent parameters which can differ both within the same group and in different groups. When the differences are small, the average value is quoted; different nitro-groups are designated by primes.

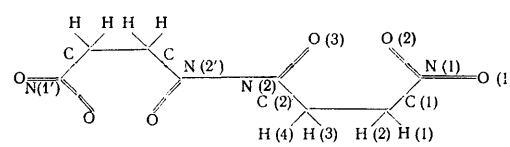
*$r(N=O)$ = 1.262(4) Å in the nitroso-group; $r(C-N_{nitroso})$ = 1.470(5) Å.

**The $N_{NO_2}CN_{NO_2}$ are 107.2(0.8)°, 107.1(0.8)°, and 104.8(0.8)°.

***The parameters of compounds (VI) and (VII) agree within the limits of the errors and average values are quoted here.

In two instances there are considerable deviations of the C–N bond lengths from the mean. An unusually long $C-NO_2$ bond [1.617(6) Å, cf. CX_3NO_2] has been found in the *o*-(phenylcyanonitromethyl)benzoylcyanoxime molecule[45], which led the authors to the conclusion that the $C-NO_2$ bond is weakened, which was confirmed by mass-spectrometric data. The $C-NO_2$ bond in 2-(nitromethylene)piperidine[51], where the nitro-group is linked to a carbon atom of the type $=C\diagup$, is shortened to 1.362(8) Å, which is smaller by 0.1 Å than in aromatic nitro-compounds. The ONO angle also is unusually small [117.7(0.6)° (the deviations of the parameters of the CNO_2 groups are not discussed by Kokkou and Rentzeperis[45])]. The nitro-group is in the *cis*-position relative to the nitrogen atom of the ring.

We shall consider certain conformational features of the compounds investigated. The dimer of 2-nitronitrosoethane[44]



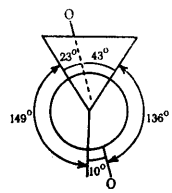
has the *trans*-configuration with the centre of symmetry in the middle of the N–N bond. In the monomeric fragments a staggered conformation is observed with projection of the C(1)–N(1) bond approximately on the bisector of the H(4)C(2)N(2) bond. This conformation is stabilised (according to Ref.44) by intramolecular interactions between the negatively charged oxygen atom O(2) of the nitro-group and the positively charged nitrogen atom (2) and by similar interactions between N(1) and O(3). The N(2)...O(2), N(1)...O(3), O(1)...O(3), and N(1)...N(2) distances are greater than the sums of the van der Waals radii. The N–N bond length [1.304(4) Å] agrees with the value found for other nitroso-compounds, for example, *cis*-nitrosomethane (1.31 Å),[54] *p*-bromonitrosobenzene (1.31 Å),[56] and potassium dinitrososulphite (1.30 Å).[56]

The plane of the NO_2 group in *O*-(phenylcyanonitromethyl)-benzenecyanoxime[45] makes a dihedral angle of 83° with the plane of the main atomic chain C′–O′–N=C and a 75° angle with the plane of the benzene ring attached to the C′ atom.

The conformations of the $C-C(NO_2)_3$ fragments in compounds such as *N*,*N*′-bis(β,β,β-trinitroethylurea[46] and *N*-(2,2,2-trinitroisopropyl)amides of chloro- and bromoacetic acids[53] are on the whole similar to the conformations

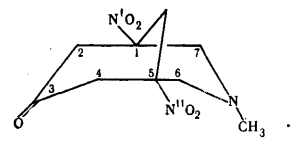
of the trinitro-compounds investigated in the gas phase. Thus the nitro-groups in the $CH_2XC(O)NHC(CH_3)C(NO_2)_3$ molecules[53] form a propeller" configuration. A relative disposition of the nitro-groups in the $OC[NHCH_2C(NO_2)_3]_2$ molecule has been indicated such that the three N...O distances between the nitrogen and oxygen atoms of neighbouring nitro-groups are reduced to 2.56 Å compared with the sum of the van der Waals radii (2.80 Å). Other N...O and O...O distances are equal to or greater than the sum of the van der Waals radii.

For alicyclic nitro-compounds, it is important to elucidate the disposition of the nitro-group relative to the ring. The determination of the conformation of the nitrocyclopropane fragment in the 6-hydroxymethylene-1,3-dinitro-*N*-oxy-3,4-methanonortropane molecule[49] yielded the results illustrated below on a Newman projection:



The same conformation of the nitrocyclopropane fragment has been found in 6,6-dibromo-2,3 : 4,5-dimethano-2,4-dinitrocyclohexanone[54].

The relative orientations of the nitro-group and the five-membered ring in the 3,5,5-trimethyl-2-nitrocyclopentanone molecule[50] are determined by the CCNO dihedral angles, which are approximately 60°. Accordingly, the angle between the planes of the ring and of the nitro-group is 95°, i.e. the nitro-group is almost perpendicular to the cyclopentane ring. The ring has the form of a slightly twisted "half-chair" with C_1 symmetry. The nitro-group and the nearest CH_3 group are in the *trans*-positions. Different orientations of the nitro-groups relative to the bicyclononane skeleton have been observed in 1,5-dinitro-3-azabicyclo[3,3,1]nonan-7-one,[55] for which two modifications have been investigated—A (space group $P2_1/c$) and B (space group $Pccn$).



The $N'O_2$ group virtually eclipses the C(1)–C(2) bond in A and B, while the other nitro-group is perpendicular to the C(5)–C(4) bond in A and eclipses the C(5)–C(6) bond in B. Thus the molecules of modifications A and B are conformational isomers.

Table 5 also presents data for the molecules of two derivatives of 5-nitrocyclopentadiene[52]. The $C-NO_2$ bond lengths in these molecules (1.43 Å) are somewhat smaller than in nitrobenzenes (1.47 Å); the remaining parameters of the CNO_2 group are closer to the parameters of aromatic rather than aliphatic nitro-compounds. In the five-membered ring the C(3)–C(4) bond length (1.446 Å) is similar to that of the $=C-C=$ bond in cyclo-octatetraene[3], while the remaining bond lengths are the same within the limits of the errors (the average bond length is 1.396 Å). The enolic hydrogen atom is midway between the two oxygen atoms and forms a short symmetrical intramolecular O...H...O bond, the O...O distance being 2.43–2.45 Å. A fairly complex picture is observed for the anions of aliphatic nitro-compounds. The structure of mononitrocarbanions has been investigated[56–58]. The parameters of the CNO_2 group in these compounds, i.e. $r(N=O)$ = 1.25–1.32 Å, $r(C-N)$ = 1.37–1.39 Å, and $\angle ONO$ = 117–121°, are significantly altered compared with the values found for neutral nitro-compounds, which can be attributed to the distribution of the charge of the anion[57].

The nitroacetate dianion $[OOC-CH-NO_2]^{2-}$ has a planar structure[56]. The atoms of the phenylnitroacetonitrile anion[57]

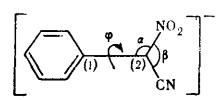


Table 6. Structural parameters of certain carbanions of the type $[R-C(NO_2)_2]$.

R	Cation	C–N	N=O	∠NCN	∠CNO	∠ONO	φ	τ	Refs
–CN	K^+	1.394	1.238	123.7	122.5	122.0	7; –7	~0	[59]
–CN	Rb^+	1.377	1.240	125.2	121.5	121.0	2.7; –5.5	~0	[60]
$-C(NO_2)_2$	K^+	1.390	1.245	121	121	120	13; 6.3	63	[61]
$-C(NO_2)_2$	Rb^+	1.380	1.243	122.5	122.6	120.5	4.1; 6.1	68	[62]
$-CONH_2$	Rb^+	1.35	1.255	123	123.5	120.5	2; 5	79	[46]
$-CH=CHCONH_2$	K^+	1.389	1.248	120.0	122.5	119.5	0; 0	0	[61]
$-C(C\equiv N)(CH_3)_2$	K^+	1.43	1.27	119	121	119	0; 30	—	[64]
$-CH_2-C(NO_2)_2(CH_2)_2C(O)CH_3$	Rb^+	1.37	1.24	120	125	113	0; 4	~90	[44]
$-C_6H_5$	K^+	1.40	1.275	120	124	119	~10; ~10	62	[46]
$-C_6H_4Cl$	K^+	1.389	1.256	119.8	123.6	120.5	10; –7	71	[65]
$-C_6H_2(NO_2)_3$	Rb^+	1.38	1.24	122	121	118	0; 0	60	[66]
$-NO_2$	$N_2H_5^+$	1.391	1.231	124.3	120.4		–7; –8	71	[46]
$-NO_2$	$N_2H_5^+$	1.371	1.239	127.2	120.7		5; 3	74	[46]

Note. The average values of the bond lengths (Å) and valence angles (degrees) in the $C(NO_2)_2$ group are quoted; ϕ are the angles of rotation of the nitro-group; τ is the angle of rotation of planar $C(NO_2)_2$ groups about the C–C(N) bond. The accuracy of the determination of the bond lengths is to within not more than 0.02 Å and that of the angles is to within not more than 2°; the data for a series of salts, obtained with a lower accuracy, are not included in the Table. In the salt of *N*-methyl-α,α-nitroacetamide (R = $CONH_2$) one nitro-group is coplanar with the amide group, while the other forms an angle of 53° relative to the latter[63].

are located in virtually two planes—those of the cyanonitromethyl fragment and of the benzene ring. The angle of rotation of the benzene ring relative to the $O_2N-C-CN$ plane is 17°. The angle α is increased to 130(3)°, while the angle is compressed to 111(3)°. The O...C(1) distance (2.87 Å) is then reduced compared with the sum of the van der Waals radii. It has been noted[58] that the geometry of the anion $[O_2NC(CN)_2]^-$ is very sensitive to the environment (in the present instance owing to the coordination to the Ag^+ ions).

The structure of the salts of polynitro-compounds containing a carbanion of the type $[R-C(NO_2)_2]^-$, including the trinitromethyl anion $[C(NO_2)_3]^-$ (R = NO_2), has been studied in greatest detail (Table 6). The parameters of the $C(NO_2)_2$ group in the carbanion differ significantly from those for the usual aliphatic nitro-compounds. Thus the C–N bond length is smaller by approximately 0.1 Å than the usual value and the CNC angle is unusually large (>120°). Appreciable differences have been observed for r(N=O) and ∠CNO. In many instance the N=O bond lengths were found to be unequal within the same nitro-group (by up to 0.06 Å).

As a rule, the $C(NO_2)$ group is almost planar and the rotations of the NO_2 groups relative to the plane are small (up to approximately 10°). The shortest O...O distance between neighbouring nitro-groups is approximately 2.6 Å. The increase of the "inner" CNO angles compared with the "outer" angles by approximately 6° is consistent with the hypothesis that the oxygen atoms of the two nitro-groups repel one another. The influence of the bulky substituent $(CH_3)_2CCN$, incapable of conjugation, on the deviation of the nitro-groups from coplanarity has been examined in relation to the anion of 2,2-dimethyl-1,1-dinitropropionitrile[64]. One of the nitro-groups has been rotated by the angle $\phi = 30°$ relative to the C–N bond, which the authors[64] attributed to the mutual repulsion of the oxygen atoms of this nitro-group and the atoms of the methyl group.

Studies of the salts $X[C(NO_2)_3]$ (X = N_2H_5,[46] K,[67] Rb,[61] or Cs [68]) have shown that the nitro-groups of the trinitromethyl anion are non-equivalent, two being located in virtually the same plane, while the third forms an angle relative to this plane.

General analysis of structural data for the anions of aliphatic nitro-compounds leads to the conclusion that the structure of the anion in the crystalline state is determined by a number of factors, among which crystal packing, intermolecular steric interactions, coordination, etc. play a significant role. It is noteworthy that unfortunately the accuracy of many studies of the salts of nitro-compounds has been low.

2. Aromatic Nitro-Compounds

Aromatic nitro-compounds constitute the largest group of nitro-compounds whose structure is now known (Table 7). It has been noted that, under the influence of the nitro-group, the geometry of the benzene ring changes, namely the inner angle at the carbon atom, to which the nitro-group is attached, as a rule exceeds 120°. This has been accounted for by the electron-accepting properties of the NO_2 group, which alter the hybridisation of the carbon atom[107]. The influence of various functional groups, including the nitro-group, on the geometry of the benzene ring has been most thoroughly examined by Domenicano et al.[108] and by Zvonkova[109] on the basis of a statistical analysis of extensive experimental data.

The method involving the statistical treatment of experimental data has been applied also by the authors of the present review to the analysis of parameters of aromatic nitro-compounds such as $r(C\cdots C)$ and $\angle CC_{NO_2}C$ in the benzene ring and the parameters of the CNO_2 group, i.e. r(N=O), $r(C-NO_2)$, and ∠ONO.[110] When the number of structural data is large, this approach can reveal the fundamental characteristics of the geometrical structure of the class of compounds under consideration.

In connection with the problem of the mutual influence of atoms and groups of atoms in molecules, nitro-compounds containing the amino-group or a chlorine atom as substituents, the data for which are more numerous than those for other substituted nitro-compounds, have been of special interest. Accordingly statistical analysis has been performed for three groups of compounds: group I—compounds which do not contain the NH_2 group or a Cl atom as substituents; group II—nitro-compounds with one or several amino-groups; group III—nitro-compounds with one or several chlorine atoms. The results of the statistical treatment, presented in Table 7, have led to the following findings.

Table 7. The weighted-mean geometrical parameters of aromatic nitro-compounds.

a	$r(C\cdots C)$, Å	$r(C-NO_2)$, Å	$r(C-X)$, Å	r(N=O), Å	$\angle CC_{NO_2}C$,°	$\angle CC_XC$,°	∠ONO,°
Group I—aromatic nitro-compounds							
1	1.384 (1)	1.467 (2)	—	1.217 (1)	122.5 (0.1)		123.1 (0.1)
2	1.383 (2)	1.473 (1)	—	1.221 (1)	123.1 (0.1)	—	124.7 (0 2)
3	1.385 (2)	1.474 (1)	—	1.218 (1)	123.3 (0.1)	—	124.8 (0.1)
Mean	1.384 (1)	1.473 (1)	—	1.218 (1)	123.2 (0.1)	—	124.5 (0.1)
Group II—aromatic nitroamines							
1	1.393 (3)	1.462 (6)	1.371 (7)	1.224 (3)	122.7 (0.5)	118.5(0.5)	122.7 (0.4)
2	1.395 (7)	1.451 (8)	1.346 (16)	1.225 (4)	122.7 (0.9)	113.6(1.0)	122.8 (0.3)
3	1.402 (4)	1.470 (4)	1.322 (7)	1.231 (3)	123.0 (0.4)	116.5(0 3)	120.9 (0.9)
Mean	1.399 (2)	1.464 (4)	—	1.228 (2)	122.8 (0.3)	116.8(0.6)	121.9 (0.4)
Group III—chloronitrobenzenes							
1	1.388 (4)	1.452 (2)	1.744 (7)	1.219 (4)	122.0 (0.3)	121.4 (0.5)	122.6 (1.1)
2	1.385 (7)	1.466 (6)	1.721 (7)	1.215 (8)	122.9 (0.2)	122.0 (0.4)	123.7 (0.3)
3	1.376 (3)	1.471 (2)	1.708 (3)	1.400 (4)	121.9 (0.3)	117.0 (0.2)	120.3 (0.3)
Mean	1.380 (2)	1.468 (2)	—	1.212 (4)	122.3 (0.2)	120.3 (0.8)	124 1 (0.3)

In compounds of group I the average $C\cdots C$ bond length is 1.384 Å and is independent of the number n of nitro-groups. A similar value $r(C\cdots C)$ = 1.380 Å has been observed for compounds of group III. The results of X-ray diffraction analysis do not permit a reliable conclusion concerning variation of the $C\cdots C$ bond in the benzene ring and the influence of nitro-groups, since the values of $r(C\cdots C)$ in crystalline benzene are subject to a considerable scatter: 1.378(3) Å without allowance for thermal corrections and 1.392(10) Å when the latter are taken into account[56]. Comparison with neutron diffraction data [$r(C\cdots C)$ = 1.393(7) Å] [54] indicates a slight shortening of the $C\cdots C$ bond under the influence of the nitro-groups. This conclusion follows more distinctly from the above electron-diffraction data for $C_6H_3(NO_2)_3$ in the gas phase.

It has been noted[111] that the average length of the $C\cdots C$ bonds adjoining the NO_2 group is smaller and that of the bonds adjoining the NH_2 groups is larger than in benzene. However, the average $C\cdots C$ bond length in aromatic nitroamines (group II) is the same as in benzene in the gas phase (1.399 Å).

The above observation—the increase of the inner angles in the benzene ring at the nitro-group—has been confirmed for compounds of all three groups. The angles in the benzene ring at the amino-group are less than 120° and those at

the chlorine atom are the same as in benzene within the limits of the errors.

Comparison of geometrical parameters such as $r(N=O)$, $r(C-NO_2)$, and ∠ONO shows that $r(C-NO_2)$ in compounds of group I is greater than in those of groups II and III; $r(N=O)$ and ∠ONO are similar for groups I and III and differ from the corresponding parameters for group II and in aromatic nitroamines there is a tendency towards an increase of the N=O bond length and a decrease of the ONO angle. There have been a number of studies where the authors attempted

Table 8. Geometrical parameters of the simplest derivatives of nitrobenzene, dinitrobenzene, and trinitrobenzene in the crystalline state.

Compound	$r(N=O)$, Å	$r(C-N)$, Å	∠ONO, deg	$\angle CCNO_2C$, deg	φ,°	Refs.
Compounds with one nitro-group						
$C_6H_5NO_2$	1.208 (14)	1.486 (20)	124	125	0	[56]
p-$O_2NC_6H_4CH_3$[a]	1.243 (7)	1.482 (7)	122.8 (0.5)	122.7 (0.5)	3	[69]
o-$O_2NC_6H_4SO_2Cl$[b]	1.223 (15)	1.455 (15)	125.5 (1.1)	119.8 (1.1)	57	[46]
o-$O_2NC_6H_4OH$[c]	1.219 (7)	1.456 (7)	123.6 (0.5)	120.7 (0.5)	2	[71]
m-$O_2NC_6H_4OH$[d]	1.217 (3)	1.477 (3)	123.4 (0.2)	123.6 (0.2)	0	[74]
p-$O_2NC_6H_4OH$(α)	1.234 (6)	1.442 (6)	122.0 (0.4)	122.3 (0.4)	1,5	[54]
(β)[e]	1.242 (3)	1.450 (3)	122.8	120	8	[54]
p-$O_2NC_6H_4OC(O)CH_3$[f]	1.215 (17)	1.459 (18)	123.2	121.5	3	[75]
o-$O_2NC_6H_4CHO$	1.230 (10)	1.468 (8)	125.0 (0.6)	123.0 (0.6)	27	[54]
syn-p-$O_2NC_6H_4CHNOH$[g]	1.214 (8)	1.432 (9)	121.7 (0.6)	120.5 (0.7)	5	[78]
p-$O_2NC_6H_4C(O)CH_3$	1.220 (4)	1.466 (4)	123.3 (0.3)	121.7 (0.3)	4	[81]
o-$O_2NC_6H_4COOH$	1.219 (8)	1.466 (9)	123.6 (0.6)	124.3 (0.6)	55	[67]
m-$O_2NC_6H_4COOH$ (stable form)	1.236 (8)	1.479 (8)	123.7 (0.5)	123.7 (0.6)	22(A)[h], 5(B)	[82]
Ditto (Unstable form)[i]	1.211 (8)	1.467 (8)	122.9 (0.5)	122.6 (0.5)	3(A)[h]; 1(B)	[83]
p-$O_2NC_6H_4COOH$ [j]	1.222 (2)	1.476 (2)	124.2 (0.1)	123.3 (0.1)	14	[84]
p-$O_2NC_6H_4C(O)OC[C(CH_3)_3]_2$[k]	1.223 (7)	1.468 (7)	123.6 (0.5)	122.8 (0.5)	0	[85]
o-$O_2NC_6H_4C(O)NH_2$	1.225 (8)	1.465 (8)	124.1	122.1	47	[90]
p-$O_2NC_6H_4C(O)NH_2$	1.223 (3)	1.468 (3)	123.1 (0.2)	122.6 (0.2)	8	[91]
p-$O_2NC_6H_4CN$	1.213 (10)	1.483 (10)	123.8 (1.0)	122.7 (1.0)	10	[92]
p-$O_2NC_6H_4NNN$ [l]	1.240 (15)	1.449 (19)	121.3 (1.2)	123.0 (1.3)	4	[54]
Compounds with two nitro-groups						
m-$C_6H_4(NO_2)_2$[m]	1.248 (6)	1.493 (6)	125.8 (0.6)	123.6 (0.6)	13	[68]
p-$C_6H_4(NO_2)_2$	1.20 (1)	1.49	127	123	12	[54]
2,4-$(NO_2)_2C_6H_3OH$[n]	1.224(5)	1.448 (5)	123.7 (0.4)	122.2 (0.4)	3; 5[o]	[93]
2,6-$(NO_2)_2C_6H_3OH$	1.241 (9)	1.465 (9)	122.9 (0.6)	122.1 (0.6)	3; 13	[96]
3,5-$(NO_2)_2CH_3C_6H_2COOH$	1.225(8)	1.481 (9)	124.7 (0.6)	124.8 (0.5)	48; 39	[44]
3,5-$(NO_2)_2C_6H_3C(O)O(CH_2)_2C(CH_3)_3$[p]	1.221	1.401	123.8	123.0	—	[97]
2,4-$(NO_2)_2C_6H_3CH_2SO_2C_6H_4CH_3$	1.208 (4)	1.480 (4)	124.5 (0.3)	122.5 (0.3)	35; 10	[102]
Compounds with three and more nitro-groups						
sym-$C_6H_3(NO_2)_3$	1.207 (10)	1.477 (10)	125.1 (0.7)	123.4 (0.7)	3;28;8 (A);10;10;5(B)	[103]
2,4,6-$(NO_2)_3C_6H(CH_3)_2$	1.218 (4)	1.477 (4)	125.1 (0.3)	124.8 (0.3)	75; 36	[104]
2,4,6-$(NO_2)_3C_6H_2Cl$[q]	1.214 (6)	1.472 (6)	124.1	122.4	81; 13; 33	[105]
2,4,6-$(NO_2)_3C_6H_2OC_2H_5$	1.214 (10)	1.469 (8)	124.0 (0.6)	122.7 (0.6)	61; 3	[61]
$(NO_2)_3C_6H_2N{=}NC_6H_2(NO_2)_3$[r]	(I) 1.221 (5)	1.480 (5)	125	123	50; 15; 39	[106]
	(II) 1.211 (5)	1.482 (5)	126	123	29:1;86;37;22;53	
$C_6(NO_2)_6$	1.23	1.45	125	120	53	[68]

[a] There are also structural data for nitromesitylene[56] and pentamethylnitrobenzene[70].

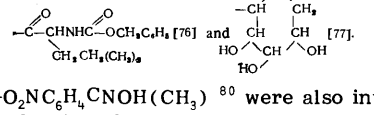
[b] The methyl ester of o-nitrobenzenesulphonic acid $O_2NC_6H_4SOCH_3$ was investigated[54].

[c] The structure of 4-chloro-2-nitrophenol was investigated[72,73].

[d] Monoclinic modification containing two independent molecules A and B in the unit cell. Their parameters do not differ within the limits of the errors. The average values are quoted here.

[e] Here α and β represent the stable and metastable modifications respectively.

[f] The p-nitrophenyl ethers $O_2NC_6H_4OR$ were investigated with the following groups R:



[g] The structures of $O_2NC_6H_4CClNOH$ [79] and p-$O_2NC_6H_4CNOH(CH_3)$ [80] were also investigated.

[h] The unit cell contains two independent molecules A and B and the average values of their bond lengths and valence angles are given.

[i] For structural data concerning 2-chloro-5-nitrobenzoic acid, see the relevant handbook[54].

[j] The structures of o- and p-nitroperoxybenzoic acids $O_2NC_6H_4C(O)OOH$ are given in handbooks[46,54].

[k] There are data for the structures of other nitrobenzoate esters of the type $O_2NC_6H_4C(O)OR$ with more complex groups R.[68,86-89]

[l] For data on o-, m-, and p-nitroanilines and their derivatives, see Table 9.

[m] For the structures of 1-chloro(bromo)-2,4-nitrobenzenes, see the relevant handbook[54].

[n] The chloro- and bromo-derivatives were investigated[94,95].

[o] Here and henceforth the angles of rotation of different nitro-groups are given; they are the same in m- and p-$C_6H_4(NO_2)_2$.

[p] The structures of several 3,5-dinitrobenzoate esters were investigated—derivatives of bicyclo-octane[46], calciferol[98,99], and toxisterol[100,101].

[q] The structure of 1,3-dichloro-2,4,6-trinitrobenzene is given in a handbook[67].

[r] I—centrosymmetric form, II—non-centrosymmetric form.

to analyse the relation between the geometrical parameters of the CNO_2 group in aromatic nitro-compounds[113–115].

It follows from Table 7 that, with increase in the number of nitro-groups in aromatic nitroamines and chloronitrobenzenes, the C–NH_2 and C–Cl bond lengths decrease.

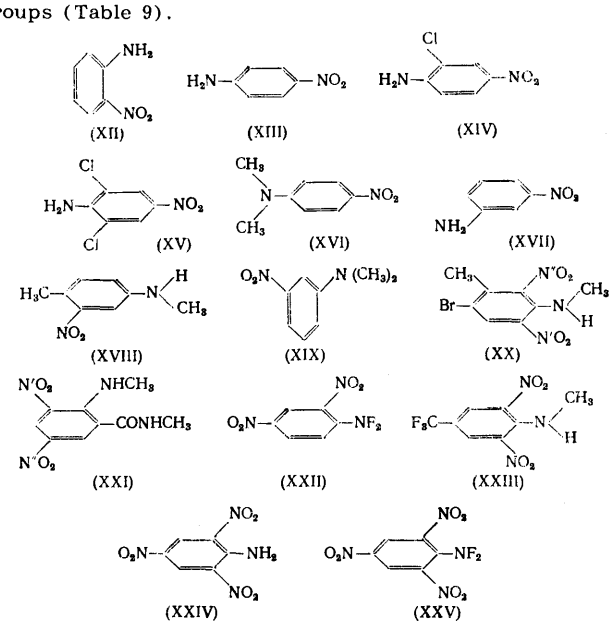
Analysis of the conformations of aromatic nitro-compounds in the crystal leads to the conclusion that the CNO_2 groups in the majority of compounds are planar or deviate insignificantly from the plane. The average CNO valence angle in the CNO_2 group is 118°, although in many cases the two angles at the same nitrogen atom have different values, apparently due to crystal field effects.

Aromatic nitro-compounds in which there are no bulky substituents next to the nitro-group have a planar or nearly planar conformation of the fragment  . Such a conformation is characteristic of *meta*- and *para*-substituted nitrobenzenes[111–116] (Table 8). In the presence of bulky *ortho*-substituents next to the nitro-group the latter rotates about the C–N bonds†. The average angles of rotation of the NO_2 groups in the absence and presence of one and two *ortho*-substituents have been calculated[116], 6°, 40°, and 63° being obtained respectively.

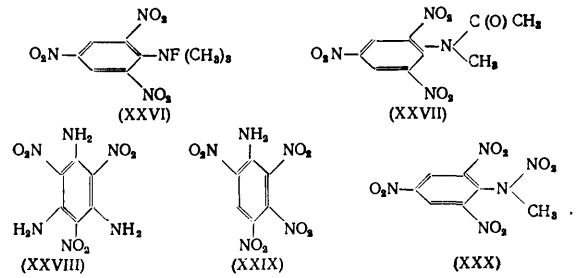
The question of the dependence of the C–NO_2 bond length on the angle of rotation of the nitro-groups has been discussed in the literature for a long time[117,118]. Such a dependence does not follow from the analysis of numerous experimental data[111]. Admittedly, the shortest C–NO_2 bonds refer to the CNO_2 groups having small angles of rotation, but the converse conclusion is not valid.

From the standpoint of the problem of the mutual influence of atoms and groups of atoms in molecules and when account is taken of the conformational characteristics, is is necessary to examine separately the structures of aromatic nitroamines, *o*-nitrophenols, polynuclear nitro-compounds, and also π-complexes of trinitrobenzene and its substituted derivatives.

The structural characteristics of aromatic nitroamines are associated with the mutual influence of the nitro- and amino-groups (Table 9).

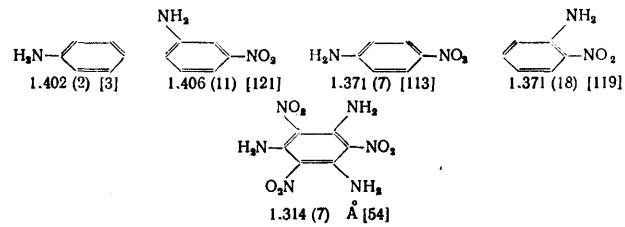


† Primary amines and phenols, in which there is a hydrogen bond, are an exception (see below).



Analysis of data for primary aromatic amines led the authors[129] to conclude that aromatic amines without the nitro-group have the longest C–NH_2 bond lengths, amines with *para*-nitro-groups have bonds of medium length, and those with *ortho*-nitro-groups have the shortest bonds.

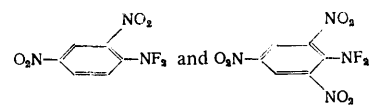
A recent X-ray diffraction study of the γ-modification of *o*-nitroaniline[119] showed that the C–NH_2 bond length in this compound is the same as in *p*-nitroaniline. An appreciable shortening of the C–Namine bonds has been observed in polynitroanilines:



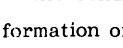
Note. Here and in the other formulae the numbers in square brackets denote references (Ed.of Translation).

The shortening of the C–N_{amine} bonds is a consequence of the influence of nitro-groups in the *o*- or *p*-positions relative to the amino-group.

The substitution of the hydrogen atoms in the NH_2 group by the more electronegative fluorine atoms leads to an appreciable lengthening of the C–N_{amine} bond to 1.46 Å, as shown by a study of

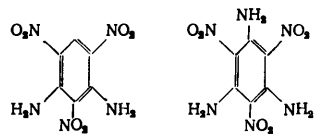


The parameters of the CNO_2 group, i.e. r(C–N), r(N=O), and ∠ONO, change less than r(C–N_{amine}), which leads to the conclusion that the effect of the interaction of the NH_2 and NO_2 groups is manifested to the greatest extent by a change in the length of the C–N_{amine} bond and is small for the CNO_2 group.

The deformations of the benzene ring caused by substituents are particularly pronounced in aromatic nitroamines[108]. The $CC_{NO_2}C$ valence angle is as a rule increased, while ∠$CC_{NH_2}C$ is reduced on average by 2–3° compared with benzene. In polynitroamines the deviations of the $CC_{NH_2}C$ angles from 120° reach 5°. In *p*-nitroaniline the C⋯C bonds in the benzene ring were found to be non-equivalent, with formation of the quinonoid structure  , the $CC_{NO_2}C$ angle is 121.4(0.4)°, and the $CC_{NH_2}C$ angle is 118.9(0.4)°.

A planar configuration of the bonds involving the amino-nitrogen atom is characteristic of *m*- and *p*-nitroanilines and their derivatives. In the absence of other substituents, the

m- and *p*-nitroaniline molecules are on the whole planar. A planar structure has also been observed for the molecule of *p*-nitroaniline and polynitroamines containing adjoining nitro- and unsubstituted amino-groups, for example;



This is associated with the formation of hydrogen bonds of the type $NH_2 \ldots O_2N$.

Table 9. The carbon–nitrogen bond lengths (Å) in the molecules of a series of nitro-derivatives of aromatic amines.

Compound	$C_{ph}-N_{nitro}$	$C_{ph}-N_{amine}$	Refs.	Compound	$C_{ph}-N_{nitro}$	$C_{ph}-N_{amine}$	Refs.
(XII)	1.490 (20)	1.371 (18)	[119]	(XXIII)	1.443 (7)	1.331 (7)	[126][d]
(XIII)	1.460 (7)	1.371 (7)	[113]	(XXIV)	1.471 (5)	1.340 (5)	[129]
(XIV)	1.471 (13)	1.386 (12)	[54]	(XXV)	1.487 (4)	1.461 (4)	[130]
(XV)	1.466 (5)	1.358 (5)	[120]	(XXVI)	1.481 (3)	1.414 (3)	[131]
(XVI)	1.405 (16)	1.358 (16)	[54][a]	(XXVII)	1.487 (3)	1.417 (2)	[132]
(XVII)	1.440 (16)	1.406 (11)	[121]	(XXVIII)	1.419 (3)	1.314 (7)	[54][e]
(XVIII)	1.474 (6)	1.377 (6)	[122][b]	(XXIX)	1.465 (6)	1.312 (6)	[68][f]
(XIX)	1.492 (1)	1.404 (9)	[123]	(XXX)	1.490 (5)	1.497 (4)	[67][g]
(XX)	CN′:1.429 (8) CN″:1.481 (8)	1.320 (8)	[67]				
(XXI)	CN′:1.456 (5) CN″:1.432 (5)	1.343 (3)	[124]				
(XXII)	1.475 (2)[c]	1.464 (2)	[125]				

[a] For structural data on 2,6-dichloro-*N*,*N*-dimethyl-4-nitroaniline, see Ref. 54.

[b] The structure of *p*-bromo-*N*-methyl-*m*-nitroaniline is also described.

[c] Here and henceforth the average values of $r(C-NO_2)$ are given.

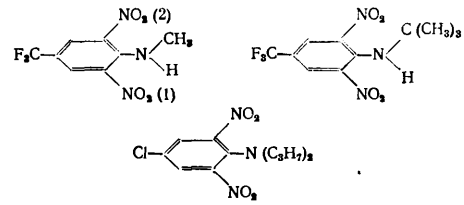
[d] The structure of Cl–C(NO₂)(N(C₃H₇)₂)(NO₂) [127] and F₃C–C(NO₂)(NHC(CH₃)₃)(NO₂) [128] were also investigated.

[e] There exist data of low accuracy (σ_r = 0.02 Å, $\sigma_\angle$ = 2°) for the 1,3-diamino-2,4,6-trinitrobenzene[67].

[f] The geometrical parameters of the $N(NO_2)CH_3$ group are $r(N-NO_2)$ = 1.348(4) Å, $r(N-CH_3)$ = 1.466(9) Å, and $\angle NNCH_3$ = 118.8(0.3)°; the angle of rotation of this group about the $C_{ph}-N$ bond is 65°.

[g] There are also data for β,β,β-trifluoroethyl-2,4,6-tetranitroaniline[44].

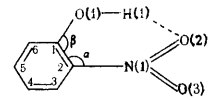
The substitution of hydrogen atoms in the amino-group by more bulky groups infringes the planarity of the molecules, as has been shown in a series of studies[126–128] of aliphatic *N*-substituted derivatives of 2,6-dinitroanilines:



The crystals of $CF_3C_6H_2(NO_2)_2NHCH_3$ contain two types of molecules whose conformations are identical: the nitro-group (1) is almost coplanar with the ring, while the nitro-group (2), closest to the methyl group, has been rotated by approximately 50°. A similar conformation has been observed in $CF_3C_6H_2(NO_2)_2NHC(CH_3)_3$. Both nitro-groups in $ClC_6H_2 \cdot (NO_2)_2N(C_3H_7)_2$ have been rotated by approximately 52° out of plane of the ring and their planes form an angle of 83° relative to one another.

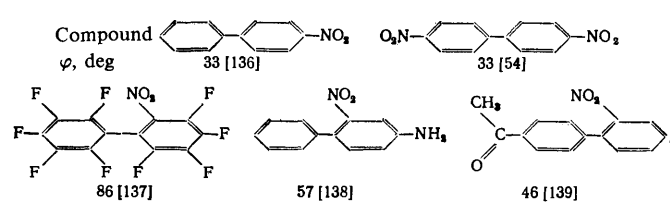
The planar configuration of the bonds involving the nitrogen atom changes to a significantly pyramidal configuration when a hydrogen atom in the NH_2 group is replaced by fluorine, i.e. in the compounds $(NO_2)_2C_6H_3NF_2$ and $(NO_2)_3 \cdot C_6H_2NF_2$. In the molecules of these compounds the nitro-groups have been appreciably rotated relative to the plane of the benzene ring.

A characteristic feature of the structure of *o*-nitrophenols (Table 8) is the formation of an intramolecular hydrogen bond between the OH and NO_2 groups. The geometry of these groups of bonds



is characterised by the following features[133]: (1) short O(1)...O(2) (2.55–2.60 Å) and H...O(2) contacts; (2) small (∠14°) angles of twist τ for rotation about the O(1)–C(1) and C–N bonds; (3) large NCC(α) and CCO(β) angles. As a rule, the N=O bonds of the nitro-group adjoining the OH group are also found to be non-equivalent: the N(1)=O(3) bond is shorter than the N(1)=O(2) bond involved in the formation of a hydrogen bond. A detailed analysis of the bond lengths in *o*-nitrophenols and nitrophenoxides has been carried out[134].

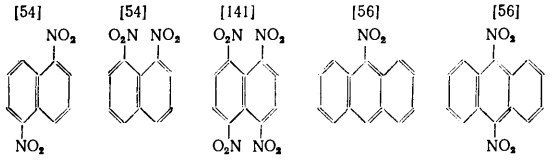
Polynuclear aromatic nitro-compounds—derivatives of biphenyl and condensed aromatic hydrocarbons—have a number of conformational characteristics. According to numerous structural data, the most significant conformational distortion of the molecules of biphenyl and its derivatives consists in the rotation (by an angle φ) of one benzene ring relative to the other about the $C_{benz}-C_{benz}$ bond[135]. The following data are available for crystalline nitrobiphenyl derivatives:



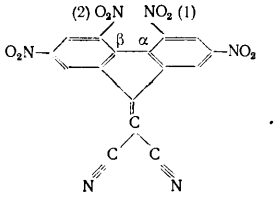
These show that the maximum angle of rotation of the ring

ϕ_{C-C} is observed in 2-nitrononafluorobiphenyl[137]#. The angle of rotation of the nitro-group in the same compound is also large (56°). A virtually coplanar disposition of the nitro-groups and the benzene ring has been noted in compounds with *p*-nitro-groups, i.e. the conformation is the same as for *p*-substituted benzene derivatives. For example, the angle of rotation of the NO_2 group in 4-nitrobiphenyl is 2°, while those in 4,4'-dinitrobiphenyl are 0° and 11°. The length of the $C_{benz}\cdots C_{benz}$ central bond in nitrobiphenyl derivatives is the same as in biphenyl (1.49 Å).

The steric hindrance in the molecules of nitro-compounds with condensed benzene rings



leads to larger angles of rotation of the nitro-groups relative to the plane of the ring and to deformations of the outer valence angles[135]. For example, the nitro-groups in 1,5-dinitronaphthalene have been rotated by 49°, those in 9,10-dinitroanthracene have been rotated by 64°, etc. The steric hindrance in 1,8-dinitronaphthalene causes the rotation of the nitro-groups by 43° relative to the plane of the ring, the displacement of the nitrogen atoms from this plane by 0.4 Å, and the deformation of the NCC valence angles by approximately 3°. The proximity of nitro-groups (1) and (2) in the 9-dicyanomethylene-2,4,5,7-tetranitrofluorene molecule[142] leads to the rotation of these groups by 35° and to an increase of the angles α and β to 123° and 134° respectively:



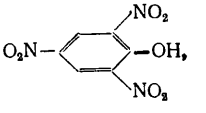
Thus in the analysis of the molecular structure of polynuclear nitro-compounds it is necessary to take into account steric factors, which frequently play a decisive role in the geometry of compounds of this class.

Unsubstituted and substituted polynitro-compounds form a series of complexes with aromatic hydrocarbons, quinhydrone, and aromatic iodo-hydrocarbons[143]. The crystal chemistry of molecular donor–acceptor π-complexes, including those of *sym*-trinitrobenzene, has been reviewed[144]. According to X-ray diffraction data, complex formation does not alter or hardly alters the molecular geometry of the donor and acceptor. In all the π-complexes of *sym*-trinitrobenzene its benzene ring is planar within the limits of experimental error, but in certain complexes, for example in the complex with acepleiadylene[68], there are slight deviations of two carbon atoms from the average plane of the benzene ring. The nitrogen atoms are also virtually in the plane of the ring. The nitro-groups are as a rule rotated by small angles (on average by 4°, at most by 18°), the angles being determined by steric effects, the packing requirements, the interaction of the donor and acceptor, etc.

The principal geometrical parameters of *sym*-trinitrobenzene in the complexes, such as *r*(C–N), *r*(C$\cdots$C), ∠ONO, and ∠CCC (according to the most accurate experimental data)[54], do not vary as a function of the donor. The significant scatter of the values of *r*(N=O) may be associated with the appreciable thermal vibrations of the nitro-group.

For the complexes of substituted trinitrobenzene derivatives, the above factors influencing the rotation of the nitro-group relative to the plane of the benzene ring are supplemented by the influence of the substituent and, as a rule, the angle of rotation of the nitro-groups in the *o*-positions relative to the substituent is much greater than for the nitro-groups in the *p*-positions.

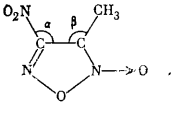
The characteristics of the structure of picric acid



which are analogous to those observed for *o*-nitrophenols and are due to the formation of an intramolecular hydrogen bond, persist in its π-complexes. The donors in these complexes are anthracene[145], pyridine[146], and 2-amino-1-bromonaphthalene[61].

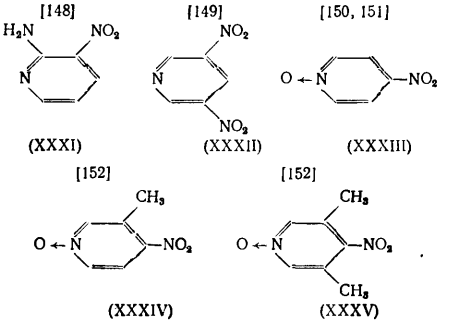
3. Heterocyclic and Organoelemental Nitro-Compounds

The heterocyclic nitro-compounds investigated are fairly varied. The nitro-group in 3-methyl-4-nitrofuroxan[147] is linked directly to the five-membered ring:



The close proximity of the NO_2 and CH_3 groups leads to conformational distortions: α = 125.7°, β = 135.3°, and ϕ_{NO_2} = 17°. The heterocyclic ring is planar with distorted valence angles. The parameters of the CNO_2 group are the same as in aromatic nitro-compounds.

The structures of derivatives of nitropyridine have been studied in greatest detail:

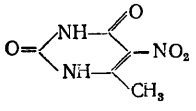


In the 2-amino-3-nitropyridine (XXXI) molecule, where the nitro-group adjoins the amino-group, one may note a decrease of *r*(C–NH_2) to 1.336 Å, similar to that observed for aromatic

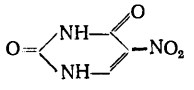
In 6,6'-dinitrophenyl-2,2'-dicarboxylic acid, which has been recently investigated[140], the angle of rotation of the rings is 71° and the angle of rotation of the *o*-nitro-groups is 30°.

nitroamines, and a slight shortening of the C–NO_2 bond to 1.440 Å. The $C_{NH_2} \cdots C_{NO_2}$ bond in the pyridine ring (1.412 Å) is somewhat longer than the other bonds in the ring (1.33–1.39 Å), while the amino-group is planar. There is an intramolecular NH...ON hydrogen bond and in the crystal the molecules are linked by NH...N_{ring} hydrogen bonds.

The molecules of 3,5-dinitropyridine (XXXII) and 4-nitropyridine *N*-oxide (XXXIII) are planar. In contrast to compound (XXXIII), the molecules of derivatives of 4-nitropyridine oxide (XXXIV) and (XXXV) are non-planar. In compound (XXXIV) the rotation of the nitro-group adjoining the CH_3 group is slight (approximately 17°). In compound (XXXV) two methyl groups are in the *ortho*-positions relative to the NO_2 group, and the angle ϕ_{NO_2} has increased to approximately 50°. It is of interest that the introduction of only one methyl group next to the nitro-group in 6-methyl-5-nitrouracil[153]



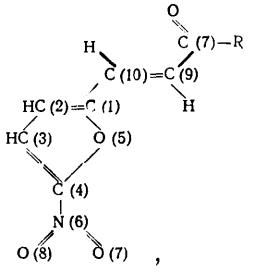
leads to the rotation of the latter by approximately 40°. The molecule of 5-nitrouracil[67]



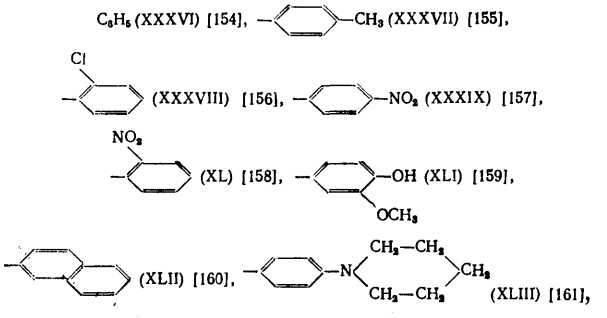
is planar.

Thus the influence of the heterocycle in the heterocyclic nitro-compounds examined hardly affects the parameters of the CNO_2 group: they are the same as for aromatic nitro-compounds.

The structure of nitrofuranylpropenes having the general formula

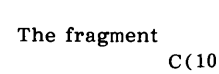


where R is

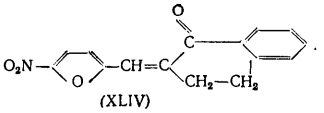


has been studied in a series of investigations[154–161].

The $C-NO_2$ bond in the CNO_2 group linked to the furan ring is shorter (1.42 Å) than in aromatic nitro-compounds on average by 0.05 Å. A slight non-equivalence of the CNO angles has been noted, but it does exceed the experimental error, the angle C(4)N(6)O(7) being greater than the angle C(4)N(6)O(8) by 2–3°. The outer angles which the nitro-group makes with the furan ring, namely ∠C(3)C(4)N(6) and ∠O(5)C(4)N(6), are respectively 130° and 117°. On the whole, the parameters of the furan ring in the compounds considered differ only slightly from those found for the furan molecule in the gas phase[3], but the ring symmetry C_2 is altered.

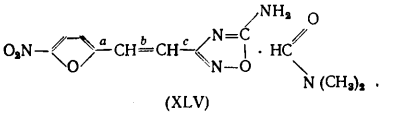
The fragment  has a cisoid configuration in the majority of compounds. The molecules of compounds (XXXVI), (XXXVII), (XXXIX), and (XLII) are planar. The non-planarity of the molecules of compounds (XXXVIII), (XL), (XLI), and (XLIII) arises only as regards the substituent R.

The series of studies examined above includes also an investigation of the molecule of compound (XLIV):[162]



(XLIV)

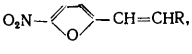
and of the complex (XLV)[163]



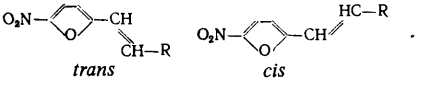
(XLV)

The parameters of the nitrofuran fragment in compounds (XLIV) and (XLV) are analogous to those discussed above. The bonds *a*, *b*, and *c* in the planar molecule of *trans*-5-amino-3-[2-(4-nitro-2-furyl)vinyl]-1,2,4-oxadiazole in complex (XLV) have the *trans*-configuration.

The structure of derivatives of 5-nitro-2-vinylfuran

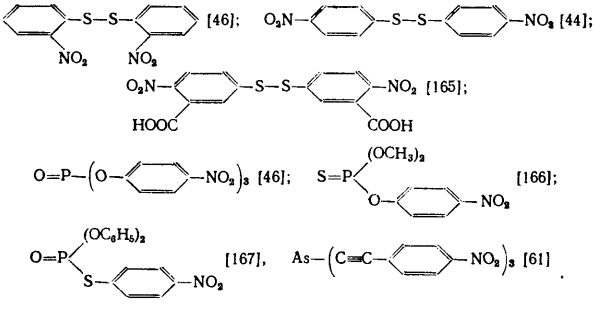


where R = $SO_2C_6H_4Cl$, $SO_2C_6H_4CH_3$, or $N(CH_3)_2$, has been investigated[164]. It has been noted that the conformation of these compounds depends on the nature of the substituent R: the *trans*-structure is preferred for compounds with electron-accepting substituents and the *cis*-structure is preferred for those with electron-donating substituents.



trans *cis*

The available structural data for organoelemental nitro-compounds are limited. The following nitro-derivatives of sulphur, phosphorus, and arsenic compounds have been studied:



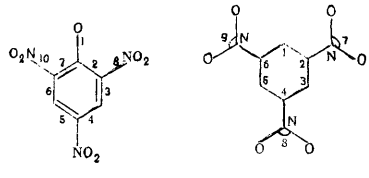
No significant deviations from the general rules governing the structure of aromatic nitro-compounds have been observed in the aromatic nitro-component.

4. Anions of Aromatic Nitro-Compounds

Changes in the geometrical parameters of the aromatic nitro-fragment have been observed in aromatic nitro-anions compared with the neutral molecules. Thus the N=O bond lengths are greater and the ONO angles are reduced to less than 120° in a series of anions. The shortening of the $C-NO_2$ bond by 0.05–0.07 Å has been noted in picrates, phenoxides, Meisenheimer salts, and certain other anions. It is believed[168] that the decrease of the length of this bond depends on the stronger interaction between the NO_2 group and the ring. The $CC_{NO_2}C$ angles in the aromatic rings of 4-hydroxy-5,7-dinitrofurazan anions[168] and in the corresponding Meisenheimer salt involving one of the nitro-groups are not increased, as is usually the case, but are actually reduced to 118.5°, which is probably associated with the influence of the furazan ring[169]. In these compounds both nitro-groups are virtually coplanar with the ring, despite the presence of the *ortho*-substituent.

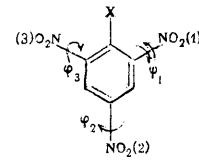
The bond lengths and valence angles in nitrophenoxides and picrates have been analysed[134] and a significant alteration of the geometry of the benzene ring in the anion has been demonstrated: bonds 2 and 7 of the C···C type have been lengthened to 1.45 Å, the CCC angle between these bonds has been reduced to 112°, and the bond lengths $r(C-O)$ and $r(C-NO_2)$ have also been altered (Table 10).

Table 10. The weighted-mean values of the parameters of nitrophenoxides and picrates (averaged with respect to 12 molecules).



Type of bond	r, Å	Type of angle	Angle, deg	Type of bond	r, Å	Type of angle	Angle, deg
1	1.248	1	111.8	6	1.370	6	124.1
2	1.451	2	123.8	7	1.444	7	121.6
3	1.373	3	119.6	8	1.452	8	122.6
4	1.380	4	121.2	9	1.445	9	120.7
5	1.384	5	119.3	10	1.443		

An interesting conformational feature has been noted on comparing the angles of rotation of the nitro-groups in picryl halides and their complexes as well as picrates[170]. It was found that in some of the compounds indicated, particularly in potassium and ammonium picrates, the nitro-groups (1) and (3) rotate in the same direction and the molecules have the C_2 symmetry with $\phi_1 = \phi_3$. In other compounds, for example, in complexes of picryl bromide with fluoranthene and pyrene, the nitro-groups (1) and (3) rotate in opposite directions and the molecular symmetry is C_S.



Comparison of the anions of aliphatic and aromatic nitro-compounds shows that the geometry of the anions of aliphatic nitro-compounds is on the whole altered less relative to neutral molecules.

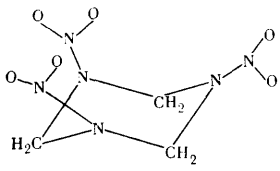
Table 11. The bond lengths (Å) and the valence angles (deg) in the nitroamino-groups in the molecules of cyclic nitro-amines*.

Molecule	r(N=O)	r(N–N)	r(N–C)	∠ONO	∠CNC
Hexogen (XLVI) (Ref.171)	1.201 (5); 1.205 (5)	1.398 (3)	1.440 (4); 1.458 (4)	125.5 (0.4)	114.8 (0.2)
	1.203 (5) 1.207 (5)	1.392 (3)	1.443 (4); 1.468 (4)	125.7 (0.4)	114.6 (0.2)
	1.209 (5); 1.233 (4)	1.351 (3)	1.450 (4); 1.464 (4)	125.0 (0.3)	115.1 (0.2)
α-Octogen (XLVIIa) (Ref.54)	1.215 (13); 1.238 (13)	1.354 (10)	1.445 (13); 1.450 (14)	125 (2)	124 (1)
	1.225 (10); 1.235 (10)	1.367 (12)	1.447 (13); 1.470 (14)	125 (2)	120 (4)
β-Octogen (XLVIIb) (Ref.56)	1.222 (8); 1.233 (8)	1.354 (5)	1.448 (7); 1.471 (6)	125.9 (0.6)	122.4 (0.4)
	1.204 (8); 1.210 (8)	1.373 (5)	1.437 (6); 1.455 (6)	126.7 (0.5)	123.8 (0.4)
δ-Octogen (Ref.172)	1.210 (25); 1.250 (15)	1.355 (23)	1.470 (23); 1.485 (19)	126.0 (1.8)	121.5 (1.4)
	1.240 (12); 1.187 (23)	1.363 (20)	1.472 (12); 1.461 (21)	121.3 (1.7)	116.6 (1.5)
	1.245 (23) 1.212 (23)	1.346 (25)	1.445 (24); 1.473 (12)	122.7 (1.9)	119.3 (1.5)
	1.201 (21); 1.113 (21)	1.392 (12)	1.500 (20); 1.442 (25)	126.3 (1.0)	119.6 (0.8)
Octogen in complex with DMF (Ref.173)	1.225 (4); 1.222 (3)	1.363 (4)	1.450 (4); 1.458 (3)	125.2 (0.3)	123.8 (0.2)
	1.220 (4); 1.217 (4)	1.377 (4)	1.459 (4); 1.453 (4)		119.7 (0.3)
(XLVIII) (Ref.174)	1.221 (2); 1.232 (2)	1.352 (2)	1.481 (2); 1.461 (2)	124.4 (0.1)	122.4 (0.1)
(XLIX) (Ref.175)	1.232 (2); 1.235 (2)	1.347 (2)	1.485 (2); 1.493 (2)	123.9 (0.2)	118.2 (0.1)
	1.225 (2); 1.223 (2)	1.386 (2)	1.485 (2); 1.490 (2)	124.3 (0.2)	113.2 (0.2)
Average values	1.221	1.367	1.463	124.9	119.3

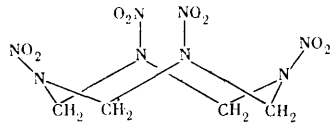
*Each row in the Table corresponds to one of the $CNNO_2$ groups.

5. *N*-Nitro- and *O*-Nitro-Compounds

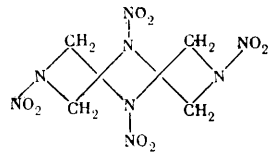
A series of *N*-nitro- and *O*-nitro-compounds, among which cyclic nitroamines occupy the principal place (Table 11), have been studied in the crystalline state.



(XLVI)



(XLVIIa)



(XLVIIб)

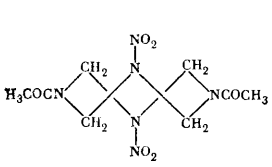
The six-membered ring of the molecule of hexogen (XLVI) has the chair conformation with two N–N bonds (1.41 Å) almost parallel with one another and approximately perpendicular to the average plane of the ring atoms; the third N–N bond (1.35 Å) is located in this plane. The molecular symmetry is C_1. The angle by which the N–N bonds are displaced from the C–N–C plane are 21.5°, 33.0°, and 32.4°. We may note that in solution the hexogen molecule has the C_3 symmetry ($\gamma = 0°$).[176]

Four crystalline modifications (α, β, γ, and δ) of octogen (XLVII) are known. The structures of α-, β-, and γ-octogens have now been determined. The crown conformation has now been established for the molecule of α-octogen (XLVIIa). Two nitroamino-groups have the equatorial conformation, while two others have the axial conformation. The planes of the neighbouring nitroamino-groups are almost perpendicular to one another. The dihedral CNNO angles are 4° and 10°.

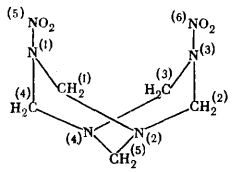
The crystal structure of β-octogen (XLVIIb) was first investigated by X-ray diffraction in 1955 [56] and was revised in 1963.[54] In 1970 the crystal structure of β-octogen was investigated by neutron diffraction[46] and it was established that the eight-membered ring of this compound has the twisted chair configuration. The $CNNO_2$ fragments of the molecule are almost planar (the dihedral CNNO angles are 0° and 10°). The angles by which the N–N bonds are displaced from the CNC planes are 4° and 17°. The two neighbouring nitroamino-groups are located in mutually perpendicular planes. In the methylene groups the HCH plane is perpendicular to the NCN plane. All the hydrogen atoms are close to the neighbouring oxygen atoms and some of them form intramolecular and intermolecular hydrogen bonds of the type CH...O.

The δ-octogen molecule resembles that of α-octogen. The $C_2N–NO_2$ groups are almost planar; the four carbon atoms of the ring lie in the same plane; the axis perpendicular to this plane is a twofold axis (we may note that the α-octogen molecule has a C_2 crystallographic symmetry). The study of the complex of octogen with dimethylformamide (DMF) [174] showed that its octogen molecule has a C_2 crystallographic symmetry and is similar in form to the molecules of the α- and δ-modifications. It is characterised by parameters which are comparable to those found for α-, β-, and δ-octogens. The nitroamino-groups are almost planar.

The structure of 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetra-azacyclo-octane (XLVIII) has been determined[175].



(XLVIII)



(XLIX)

As for β-octogen, the same C_1 molecular symmetry and twisted chair conformation have been established. The C and O atoms of the $COCH_3$ group and the NO_2 group are located in the same plane with the nitrogen atoms to which they are attached. The bond lengths and valence angles in the molecule of compound (XLIII) are close to those found for α-, β-, and δ-octogens.

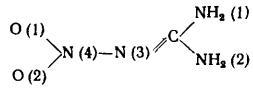
The cyclic nitroamine 3,7-dinitro-1,3,5,7-tetra-azabicyclo-[3,3,1]nonane (XLIX) [176] is an intermediate in the synthesis of octogen and hexogen. The molecule of this compound contains the eight-membered C,N-ring of octogen and the six-membered C,N-ring of hexogen. The two NNO_2 groups are planar. The dihedral angles between the NNO_2 and CNN planes are 26° and 34°. The molecule has an approximate plane of symmetry passing through the N(5), N(1), C(5), N(3), and N(6) atoms. The molecule is structurally more similar to hexogen than to octogen. Table 11 shows that the C–N bonds in the nitroamino-groups of compound (XLIX) are longer by 0.02–0.05 Å than in octogen and hexogen. The CNC angles, which are on average 115.6°, are much smaller than the corresponding angles in octogen, but agree with the angles in hexogen.

There are a number of structural data for open-chain nitroamines: NH_2NO_2;[56] $(CH_3)_2NNO_2$,[56] and $O_2NNHCH_2CH_2.NHNO_2$.[61] The structures of nitroamine and dimethylnitroamine have been investigated with a low accuracy. The NH_2NO_2 molecule is planar in the crystal, in contrast to the gas phase. In the crystalline state dimethylnitroamine has the same planar molecular configuration as in the gas phase, but the N–N bond length is greatly reduced [1.25(5) Å]. $CNHNO_2$ groups in the *N,N'*-dinitroethylenediamine molecule are planar, but the molecule as a whole is non-planar with a dihedral angle of 84° between the CCN and CNN planes. The N–N bond length is 1.301(4) Å.

A planar configuration of the amino–nitrogen bonds is characteristic of two *N*-substituted derivatives of tetranitroaniline (Table 9). The N–N bond length in *N*-methyl-*N*,2,4,6-tetranitroaniline (tetryl)[67] is 1.35 Å and the $N\begin{smallmatrix}NO_2\\CH_3\end{smallmatrix}$ group has been rotated relative to the plane of the benzene ring by 65°. The N–N bond in *N*,*N*-(β,β,β-trifluoroethyl)-*N*,2,4,6-tetranitroaniline[44] is longer than in tetryl (1.41 Å) and the angle of rotation of the group $-N\begin{smallmatrix}NO_2\\CH_2CF_2\end{smallmatrix}$ relative to the plane of the ring is 86°.

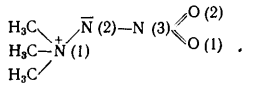
The planarity of the $-C\begin{smallmatrix}\diagup\\\diagdown\end{smallmatrix}N–NO_2\begin{smallmatrix}\diagdown\\\diagup\end{smallmatrix}C-$ group with $r(N–N)$ = 1.357(5) Å in 2,2'-dinitratoethylenenitroamine $O_2NN(CH_2CH_2.ONO_2)_2$ [177] has been established by X-ray diffraction. Other parameters of this molecule are discussed below.

The structures of a number of *N*-nitro-compounds which do not belong to the class of nitro-amines have also been studied. The nitroguanidine molecule[56]



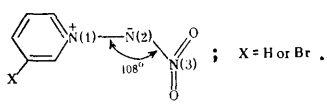
is planar with an N–N bond length of 1.35(1) Å. The steric hindrance arising between the N(1) and O(1) atoms increases the O(1)N(4)N(3) and N(1)CN(3) valence angles to 124° and 129° respectively. The remaining angles do not deviate from the usual values.

The structure of trimethylammonium nitroamidate, which is an ylid, has been investigated[178]. The N(1)–N(2) bond length [1.47(1) Å] in this molecule is close to that found in hydrazine (1.45 Å), i.e. it is a single bond.

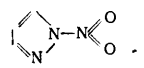


On the other hand, the bond lengths in the N–NO_2 fragment have unusual values: r(N–NO_2) = 1.32(1) Å [longer than the N=N double bond (1.25 Å) but shorter than the N–N bonds in nitroamines]; the N=O bond length [1.26(1) Å] exceeds somewhat the values usual for the NO_2 group. The authors[178] believe that this occurs owing to the considerable delocalisation in the charge in the nitro-group. The N(1)N(2)N(3)O(1) dihedral angle is approximately 0°.

In 1974 a large group of investigators published structural data for two representatives of heterocyclic *N*-nitroimides–pyridine 1-nitroimide and its bromo-derivative[179].



In these compounds the $\overset{+}{N}-\overset{-}{N}-NO_2$ system is almost planar and the dihedral angle relative to the plane of the ring is 72° for unsubstituted pyridine 1-nitroimide and 78° for its bromo-derivative. The bond lengths r(Å) are 1.42, 1.34, and 1.25 for N(1)–N(2), N(2)–N(3), and N=O respectively. Compared with the $(CH_3)_3\overset{+}{N}-\overset{-}{N}-NO_2$ system, the N(1)–N(2) bond is considerably shorter, the N(3)–N(4) bond is lengthened, and the NNN angle is reduced. We may note that the N(2)–N(3) bond length in this compound is close to r(N–N) in cyclic nitroamines. *N*-Nitropyrazole[180] also belongs to the class of compounds containing the N–NO_2 bond.

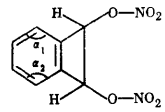


The molecule is planar and the N–NO_2 bond length (1.399 Å) and the ONO angle (128.5°) are somewhat increased relative to the average values of these parameters in crystalline nitroamines. The N–C (1.364 Å), N=C (1.315 Å), C=C (1.341 Å), and C–C (1.407 Å) bond lengths in the pyrazole ring differ from the corresponding bond lengths in unsubstituted pyrazole[3] by 0.01–0.03 Å.

Few X-ray diffraction data are available for *O*-nitro-compounds. The compound $O_2NN(CH_2CH_2ONO_2)_2$, which has been investigated[177], contains both the N–NO_2 and O–NO_2 groups with bond lengths of 1.357(5) and 1.399(6) Å respectively. The O=N=O angle in the nitroxy group (approximately 130°) is much greater than in the nitroamino-group (125°). The atoms of the molecule are located in three planes: one plane contains the atoms of the nitroamino-group $O_2N-N\begin{matrix}C\\C\end{matrix}$ and the other two planes contain the atoms of the $CONO_2$ groups.

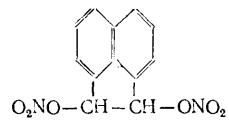
Two crystalline modifications of pentaerythritol tetranitrate $C(CH_2ONO_2)_4$ have been investigated—the low-temperature[54] and high-temperature[181] modifications. The geometrical parameters of the $CONO_2$ groups in both forms are close to the corresponding parameters of the CH_3ONO_2 molecule.

X-Ray diffraction analysis confirmed that the high-boiling isomer of benzocyclobutene 1,2-dinitrate[146] has the *cis*-configuration:



An interesting feature of the structure of this compound is the reduction of two angles in the benzene ring (α_1 and α_2) to 115°. Similar deformations of the angles have also been noted for other benzocyclobutene compounds. The bond common to the two rings (1.363 Å) has been shortened by approximately 0.02 Å relative to the average $(C\cdots C)_{benz}$ bond length, which is 1.383 Å. The length of the C(1)–C(2) bond in the cyclobutene ring is 1.561(5) Å. The nitrate groups are planar and have been rotated relative to the plane of the ring by 53° and 71°.

The dinitrate of *cis*-acenaphthene-1,2-diol



has a similar structure. The planar nitroxy-groups in this compound are inclined to the plane of the carbocyclic ring at angles of 62° and 72°.

In conclusion of this section we should note that in the cyclic nitroamines investigated the configuration of the bonds involving the nitrogen atom is planar or nearly planar. The average parameters are presented below (r in Å; the angles are expressed in degrees):

r(N=O)	r(N–N)	r(N–C)	∠CNO	∠CNC
1.221	1.367	1.463	124.9	119.3

In nitric acid esters the nitrate groups C–O(1)–N$\begin{matrix}O(2)\\O(3)\end{matrix}$ are as a rule planar with the following parameters:

r(N=O)	r(N–O(1))	r(C–O)	∠O(2)NO(3)	∠O(1)NO(2)	∠O(1)NO(3)
1.20	1.40	1.45	130	117	112

The differences between the O(1)N=O angles, which are outside the limit of the experimental error, have been explained by the steric repulsion of the C and O(2) atoms.

IV. CONCLUSION

Inspection of the combined data on nitro-compounds shows that there are distinct differences in the geometries of the NO_2 group in molecules of compounds of different classes. The N=O bond lengths vary in the range 1.20–1.24 Å with an average of 1.22 Å and the ONO valence angles vary in the range 123–133° with an average of approximately 128°. The minimum ONO angles are observed in molecules of aromatic nitro-compounds and nitroamines, while the maximum values are observed in molecules of aliphatic and alicyclic nitro-compounds. This is apparently associated with the fact that in aromatic nitro-compounds and nitroamines carbon atoms or amino-nitrogen atoms with a planar bond system are linked to the NO_2 group. The tendency towards an overall planar configuration of the NO_2 group and the groups linked to it in these molecules gives rise to a steric strain, which leads to a decrease in the ONO angle.

Analysis of structural data on aliphatic and aromatic nitro-compounds leads to the conclusion that the C–N bond lengths in the molecules of aliphatic compounds (average

1.51 Å) are greater by 0.03–0.04 Å than in the molecules of the aromatic compounds (average 1.47 Å). Similar variations are observed also in the C–C(=O)R bond lengths. The lengths of the >C–C(=O)R bonds are greater than those of >C–C(=O)R (or >C–C(=O)R) bonds by 0.03 Å.

Previously, when only a limited amount of data on the structure of nitro-compounds was available, it was noted that the lengths of different types of >C–NO_2 and >C–NO_2 bonds are equal[36]. Nowadays this conclusion must be regarded as erroneous.

Statistical analysis of the C–N bond lengths and ONO valence angles indicates a correlation between these quantities. With increase of the ONO valence angle, the C–N bond length as a rule also increases.

The planar conformation of nitroamines and aromatic nitro-compounds, in which there are no appreciable steric interactions, confirms the idea that the nitro-group is conjugated with the amino- and phenyl-groups. This is also confirmed by the finding that the amino-nitrogen atom has a planar bond configuration in contrast to the pyramidal bond configuration in the simplest amines. The effects due to the transmission of influences through the benzene ring to the *para*-position have also been observed in aromatic nitro-compounds. Steric interactions lead to the breakdown of the planar conformation of the >N–N(=O)=O and >C–N(=O)=O fragments. It is noteworthy that the >C–N(=O)=O bond length has not yet been found to vary with the angle of rotation about the C–N bond.

In aliphatic compounds the NO_2 group also influences the neighbouring bonds, but is nature is somewhat different. The conformations of the molecules of aliphatic nitro-compounds depend to a large extent on the type of groups attached to the carbon atom and on the number of nitro-groups. For a deeper understanding of the characteristics of the geometrical structure of the molecules of nitro-compounds, systematic studies are necessary.

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The Charge-transfer Complexes of Neutral Donors with Organic Cations as Acceptors

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The principal results of studies on charge-transfer π-complexes (CTC) with an organic cation (carbonium, heteroaromatic, and hetero-onium) as the acceptor are examined and problems of the classification of the CTC on the basis of the structures of the ground and excited states are discussed. The thermodynamic and spectroscopic data for the type of CTC considered are analysed. The results of the determination of the electron affinities of the acceptor cations are examined and surveyed. Ideas concerning the photochemical properties of the CTC or arenediazonium ions, which are of interest as materials for the recording of information, are described.
The bibliography includes 101 references.

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I. INTRODUCTION

The chemistry and physics of charge-transfer complexes (CTC) now constitute in many respects an independent field, which is closely related to a number of other fundamental scientific disciplines as well as practical applications[1]. Despite the fairly large number of reviews and books on this field[2-12], some types of the CTC have been described extremely superficially. These include also the CTC formed by a neutral electron donor and an acceptor cation. Although the specific conductances of crystalline CTC of this type[13-15] are fairly low, one cannot claim that their interaction is of no practical interest. It is known that many acceptor cations are directly involved in important biological processes[4] or exhibit a pronounced biological activity[12,13,16,17]. Charge-transfer complexes with a nitronium cation are considered as intermediates in the nitration of aromatic compounds[18,19] and the CTC of diazonium salts are believed to be a possible means of improving the light sensitivity of photographic materials[20,21]. From this, it follows that the comparatively little investigated type of CTC formed between a neutral π-donor and an acceptor cation is fairly interesting also from the practical point of view.

The aim of the present review is to examine the general characteristics of the formation of the CTC of this type; particular attention has been devoted to the electron affinities of the acceptor cations and the photochemical properties of the CTC of diazonium salts. The complexes between aromatic hydrocarbons and metal cations are not considered

here; the readers interested in this problem are recommended to refer to the interesting monograph of Mulliken and Person[5].

II. THE ENERGY LEVEL SCHEMES AND THE CLASSIFICATION OF THE CHARGE-TRANSFER COMPLEXES

The formation of CTC is usually accompanied by the appearance of one or several new bands in the electronic absorption spectrum. These bands are referred to as the charge-transfer (CT) bands and are due to the intermolecular electronic transition on excitation of the CTC. Despite the fact that the presence of CT bands in the spectrum is not in general proof of the formation of a thermodynamically stable CTC and their absence does not rule out the formation of such a complex, nevertheless CT bands are the most characteristic feature of the absorption spectra of CTC. The charge-transfer energy depends on the ionisation potential of the donor $IP(D)$, the electron affinity of the acceptor $EA(A)$, and the stabilisation energies of the ground and excited states of the CTC.[5] The electronic transitions for different components of the CTC can be represented schematically as follows:

$$D, A \xrightarrow{h\nu_{CT}} D^{+}, A^{-} \qquad (I)$$

$$D, A^{+} \xrightarrow{h\nu_{CT}} D^{+}, A^{\cdot}. \qquad (II)$$

The fundamental differences between the stabilisation energies of the CTC formed by two neutral molecules [reaction (I)] or an ion and a neutral molecule [reaction (II)] follow from this approximate scheme. In the first place the excited state is stabilised by the strong Coulombic interaction of the oppositely charged species, while in the second case this does not occur. The different structures of the ground and excited states of the above CTC make it possible to refer them to two separate types of CTC.[22] The energy levels arising on their formation are presented in Fig.1. Weak CTC, in the formation of which the contribution of the CT forces is insignificant, are considered in both cases.

The CT energies for CTC of both types in the gas phase are expressed by the following equations:

$$h\nu_{CT}(D, A) = IP(D) - EA(A) + (W_0 - E_c) + (R_N + R_E), \qquad (1)$$

$$h\nu_{CT}(D, A^{+}) = IP(D) - EA(A^{+}) + (W_0' - W_1) + (R'_N + R'_E), \qquad (2)$$

where W_0, W'_0, W_1 are the stabilisation energies of the ground and excited states as a consequence of all the types of interaction with the exception of the interaction via the charge-transfer pathway, E_C is the Coulombic interaction energy of the oppositely charged species, and R_N, R_E, R'_N, and R'_E are the energies of stabilisation or destabilisation as a consequence of the interaction of the configurations without charge transfer and with complete charge transfer in the ground (N) and excited (E) states respectively. Assuming that for a weak CTC the sums $R_N + R_E$ and $R'_N + R'_E$ are small and approximately equal, we conclude that the constant terms in Eqns.(1) and (2) are largely determined by the differences $W_0 - E_C$ and $W'_0 - W_1$ respectively. The upper limit to the quantity W_0 is set by the experimental ΔH, which do not exceed 0.5 eV for the CTC of tetracyanoethylene with methylbenzenes and naphthalene in the gas phase[10]. According to theoretical estimates[5], the quantity E_C exceeds somewhat 3 eV. Thus $W_0 - E_C \cong -3$ eV and we obtain from Eqn.(1)

$$h\nu_{CT} \simeq IP(D) - EA(A) - 3 \ \text{(eV)},$$

which agrees fairly well with experiment[23]. When a CTC is formed between an ion and a neutral molecule, one can assume that $W_0 \geq W_1$ and the CT energy in the gas phase is approximately expressed by the equation

$$h\nu_{CT} \simeq IP(D) - EA(A^{+}) + E_{II}, \qquad (3)$$

where $E_{II} \geq 0$. According to the Franck–Condon principle, the energy is higher in solutions (Fig.1).

Thus the $h\nu_{CT}$ in the two cases examined differ greatly, the difference seeming more appreciable than the changes arising as a consequence of the difference between the types of the interacting boundary orbitals of the components (m, σ, π, etc.) for both types of CTC considered. The distinctive features of the CTC having different ground and excited states are also manifested directly in the experiment. For example, it has been established[24] that the CT energy and the formation constants of CTC vary differently with increasing pressure depending on whether the CTC are formed by neutral molecules, a neutral molecule and an ion, or two oppositely charged ions.

Because of the reasons described above, we believe it useful to classify the CTC beginning with the structures of the ground and excited states having specified three main types: (1) CTC between neutral molecules (D, A); (2) CTC between an ion and a neutral molecule (D^{-}, A and D^{+}, A); (3) CTC between oppositely charged ions (D^{-}, A^{+}). Within the limits of these types, further classification can be achieved in conformity with the type of interacting orbitals[5] and, within the limits of the resulting subtypes, also in terms of the classes of the compounds.

III. GENERAL INFORMATION ABOUT THE SPECTROSCOPIC AND THERMODYNAMIC PROPERTIES OF THE CHARGE-TRANSFER COMPLEXES BETWEEN A NEUTRAL π-DONOR AND AN ORGANIC CATION AS AN ACCEPTOR

During the period since the publication of the first studies on the CTC of the type considered[25], a comparatively small amount of experimental data has accumulated. However, the date are sufficient to reach a number of conclusions, which is facilitated by the availability of the results of analysis of extensive experimental data on the CTC between neutral species[1–12].

It has been observed that organic cations of different classes of compounds are capable of forming CTC with neutral π-donors. The cations include carbonium ions (tropylium, triphenylmethyl, and diphenylmethyl cations), heteroaromatic ions (protonated and alkylated N-heterocycles, derivatives of pyrylium and thiopyrylium), and hetero-onium ions (diaryliodonium and arenediazonium ions). So far it is not altogether clear what causes the complex-forming capacity of diaryliodonium ions, since only the formation of their CTC with aromatic amines[26], which are capable of utilising their l orbitals for the interaction, has been reported. For the remaining cations, the CTC with pure π-donors have also been studied.

The complex-formation constants K of CTC in solution are usually low and vary in the range 1–10 litre mol^{-1} depending on the properties of the CTC components and the solvent (Table 1). The individual instances where the constants K are much greater than 10 litre mol^{-1} are either associated with specific conditions promoting complex formation or can be accounted for by experimental difficulties in their correct determination[10].

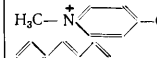
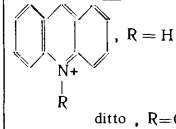
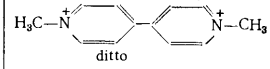
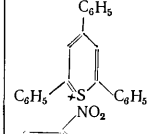
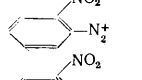
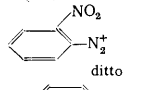
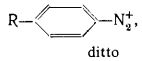
In most cases the constants K for neutral donor–cationic acceptor CTC are similar to those for weak $\pi-\pi$ CTC of neutral molecules. As for the latter, there is a tendency towards an increase of K with decrease of the ionisation potential of the donor and with increase of the electron affinity of the acceptor (see Nos.1–4 and 17–25 in Table 1).

However, this tendency does not constitute proof of the predominant contribution of the CT forces[5,10] and there are at present no grounds for the belief that CT forces are the main ones in complex formation. It is most likely that the degree of charge transfer in the ground state is slight and complex formation is determined to a larger extent by the forces of universal intermolecular interactions than by CT forces. Nevertheless the question of the contribution of the CT forces to the formation of CTC of the given type must be regarded as open in view of the inadequacy of the experimental data. The problem of whether CTC of the given type are contact or thermodynamically stable complexes has been studied more widely. The CTC of the given type are thermodynamically stable, since the enthalpies of complex formation ΔH are negative (Table 1). The absolute value of ΔH does not exceed 6 kcal mol^{-1}, which is characteristic of weak $\pi-\pi$ complexes of neutral molecules[5,10]. Like the latter, the CTC between a neutral donor and a cationic acceptor can be obtained in a crystalline state[13-15,27,31,32,35].

In most cases a more or less distinct CT band is observed in the electronic spectrum of the CTC. The CT energy is usually determined from the maximum of the CT band, which in the general does not correspond to the 0–0 transition. Determination of the CT energies for the 0–0 transition has shown[36] that the latter vary approximately in parallel with the CT energies determined from the CT band maxima but are smaller by 0.35–0.4 eV. Therefore the observed dependence of $h\nu_{CT}$ on the characteristics of the components remains unaltered regardless of the way in which the CT energy has been determined.

The study of the CTC formed by identical acceptors with different donors has shown that the CT energy usually varies linearly with IP(D); this is also characteristic of CTC of other types[5,10]. The slope of the $h\nu_{CT}$–IP(D) straight lines is close to unity: for the CTC of aromatic hydrocarbons with the tropylium cation, it is 0.98 in methylene chloride[27] and 1.0 in acetonitrile[37]; it is 0.87 for the CTC of 4-cyano-*N*-methylpyridinium with polyalkylbenzenes in 96% ethanol[29] and 0.96 for the complexes with aromatic hydrocarbons in chloroform containing 8 vol.% of ethanol[38]; for the CTC of aromatic hydrocarbons with benzenediazonium cations in nitromethane, the slope is 0.92.[39,40] Such relations can be regarded as satisfactory evidence that the new absorption bands appearing in the spectrum are indeed CT bands. The slope of the above straight lines depends little on the properties of the solvent, so that the different values obtained in different studies are largely due to the different nature of the donors and their ionisation potentials.

Table 1. Thermodynamic parameters of CTC in solution.

No.	Donor	Acceptor	Solvent	K, litre mol^{-1}	ϵ_{max}, mol^{-1} cm^{-1}	$-\Delta H$, kcal mol^{-1}	T, K	Refs.
1	Anthracene		CH_2Cl_2	1.2	—	2.0	298	[27]
2	Hexamethylbenzene	ditto	CH_2Cl_2	1.1	—	1.5	298	[27]
3	Naphthalene	»	CH_2Cl_2	0.55	—	1.3	298	[27]
4	Mesitylene	»	$C_2H_4Cl_2$	0.67	1850	—	298	[28]
5	1,4-Dimethoxybenzene		C_2H_5OH (96%)	0.35	350	1.46	298	[29]
6	Anthracene		CH_2Cl_2	1.5	1020	—	294	[30]
7	Anthracene	ditto, R=CH_3	CH_2Cl_2	2.7	910	—		[30]
8	Pyrene		CH_3OH	3.4	360	—	298	[31]
9	Hydroquinone	ditto	CH_3OH	5.2	115	5.5	298	[13,31]
10	1-Naphthylamine*	»	CH_3OH	8.7	192	—	298	[31]
11	*N*-Phenyl-2-naphthylamine*	»	CH_3OH	88	42	—	293	[32]
12	*p*-Phenylenediamine*	»	CH_3OH	15.4	95	—	298	[31]
13	Triphenylamine*		CH_2Cl_2	1.1	100		293	[15]
14	Naphthalene		$CH_3COOH:H_2O=4:1$	4.4	—	—	293	[33]
15	1-Methylnaphthalene		$CH_3COOH:H_2O=4:1$	14.4	—	—	293	[33]
16	Naphthalene-1-sulphonic acid	ditto	$CH_3COOH:H_2O=4:1$	30.6	—	—	293	[33]
17	Fluorene		CH_3CN	0.56	—	—	293	[34]
18	Phenanthrene	ditto	CH_3CN	0.61	—	—	293	[34]
19	Hexamethylbenzene	»	CH_3CN	0.65	—	—	293	[34]
20	Pyrene	»	CH_3CN	0.88	—	—	293	[34]
21	Anthracene	»	CH_3CN	0.64	—	—	293	[34]
22	Pyrene	ditto, R=CN	CH_3CN	1.26	—	—	293	[34]
23	Pyrene	», R=$COOC_2H_5$	CH_3CN	1.13	—	—	293	[34]
24	Pyrene	», R=CH_3	CH_3CN	0.6	—	—	293	[34]
25	Pyrene	», R=OCH_3	CH_3CN	0.56	—	—	293	[34]

*The compounds are *l*-donors and coordination involves both the nitrogen atom and the residual π-system.

The influence of the solvent on the CT energy has been studied in a number of investigations[28,29,36,41,42]. According to the energy level scheme in Fig.1, the CT energy in the gas phase is expressed by Eqn.(2), while in solution a more complex relation obtains:

$$h\nu_{CT}(D, A^+)_{solv} = IP(D) - EA(A^+) + \\ + (W_0' - W_1) + (R_N' + R_E') + [E_{solv}(D, A^+) - E_{solv}(D^+, A^-)] + E_{FC} \quad (4)$$

Since it can be assumed with adequate approximation that the solvation energy $E_{solv}(D, A^+) \cong E_{solv}(D^+, A^-)$, the frequency shift on transition from the gas phase to the solution and also when the solvent is altered should be determined mainly by the quantity E_{FC}, i.e. $\Delta h\nu_{CT}(D, A^+) \cong \Delta E_{FC}$. In this case a comparatively slight hypsochromic shift is to be expected on passing from the gas phase to the solution as well as a comparatively weak solvatochromism in different solvents. The latter hypothesis has been confirmed experimentally (Table 2). Nevertheless there is no reason to believe that the solvent virtually does not influence the CT energy[36]. The shift of the CT band in a series of 14 solvents presented in Table 2 is approximately 2000 cm^{-1} for the majority of CTC. This quantity is small compared with the corresponding shift of the CT band for the CTC formed by oppositely charged ions (approximately 7000 cm^{-1}), but is too large to neglect the influence of the solvent. The influence of the properties of the solvent on the CT energy is confirmed also by experimental data on the solvatochromism of substances with an analogous intramolecular transition[44,45].

Table 2. The influence of the solvent on the position of the CT band maximum ($10^{-3}\nu$, cm^{-1}).

Solvent	E_T (Ref.43)	Charge-transfer complex: Hexamethylbenzene.tropylium fluoroborate (Ref.41)	Anthracene.tropylium fluoroborate (Ref.41)	Pyrene.tropylium fluoroborate (Ref.41)	Anthracene.N-methylacridinium fluoborate (Ref.41)	Dimethylaniline.4-cyano-N-(n-decyl)pyridinium fluoroborate (Ref.29)	Phenothiazine.tropylium fluoroborate (Ref.42)
Methanol	55.5	—	—	—	20.1	21.37	—
Ethanol	51.9	—	—	—	—	21.14	—
Acetic acid	51.2	24.6	20.4	20.3	—	—	16.9
1-Propanol	50.7	—	—	—	—	21.19	—
Nitromethane	46.3	24.0	20.2	—	19.9	—	—
Acetonitrile	46.0	24.2	20.6	20.5	19.9	21.62	17.0
Dimethyl sulphoxide	45.0	—	21.3	21.3*(i)	—	22.52	14.7
Acetic anhydride	43.9	24.2	20.6	20.5	20.3	—	17.0
Dimethylformamide	43.8	24.5	21.7	22.2(i)	21.5(i)	22.47	15.5
Acetone	42.2	24.3	20.8	20.8	20.2	22.2	17.1
Nitrobenzene	42.0	22.2	19.4(i)	19.3	19.5	—	15.9
Dichloroethane	41.9	22.6	18.6	18.7	19.0	—	14.9
Methylene chloride	22.9	18.7	—	19.1	20.83	—	—
Chloroform	39.1	—	—	—	19.7	21.03	—

*Here i = inflection.

There is a satisfactory linear relation between the energy shifts of the CT bands for all six CTC in Table 2. Consequently, apart from the individual instances of the specific interaction of the components or of the CTC itself with the solvent, these data contain information about the influence of

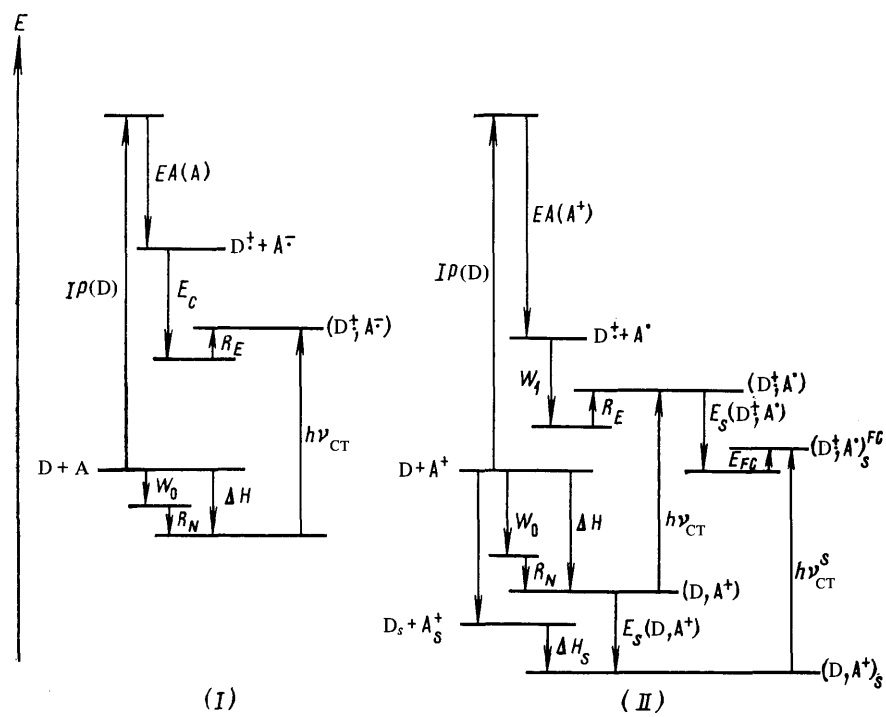


Figure 1. Schematic arrangement of the energy levels for CTC between neutral molecules (I) and a neutral molecule and an ion (II); E_C = Coulombic interaction energy; R_N, R_E = stabilisation or destabilisation energies as a consequence of the interaction of the configurations without and with complete charge transfer in the ground and excited states respectively; W_0, W_1 = stabilisation energies of the ground and excited states as a consequence of all types of interactions with the exception of CT forces; ΔH, ΔH_S = enthalpies of complex formation in the gas phase and in solution; $h\nu_{CT}$ = CT energy; $E_S(X)$ = solvation energy of the corresponding structure X; E_{FC} = destabilisation energy of the non-equilibrium excited state relative to the equilibrium state (the Franck–Condon state).

the solvent on the CTC of this class as a whole. The changes in the CT energies when the solvent is altered are not correlated with empirical parameters of the solvent such as the values of Z and E_T.[29,41,42] Nor does one observe their dependence on the polarisability of the solvent expressed in the form $(n^2 - 1)/(2n^2 + 2)$, where n is the refractive index. A quantitative description of the dependence of the CT energy on the properties of the solvent is probably possible in this case only with the aid of a multiparameter equation[43]. In broad outline, the state of the problem is very similar to that in the case of neutral $\pi-\pi$ complexes[45,46,47], although there is no correlation between the frequency shifts for the CTC of the two types. The structure of the so-called cybotactic region probably plays the most important role in both cases[4].

IV. THE ELECTRON AFFINITY OF ACCEPTOR CATIONS

The electron affinity EA is defined as the energy evolved (+) or absorbed (−) when a given species (atom, molecule, ion, radical, or radical-ion) captures an electron in the gas phase. If the species is a positive ion, then the vertical and adiabatic electron capture processes can be illustrated by the following equations:

$$A^+(r_{A^+}) + e \xrightarrow{EA_v(A^+)} A^{\cdot}(r_{A^+}), \quad (5)$$

$$A^+(r_{A^+}) + e \xrightarrow{EA_{ad}(A^+)} A^{\cdot}(r_{A^{\cdot}}), \quad (6)$$

where $EA_v(A^+)$ and $EA_{ad}(A^+)$ are the vertical and adiabatic electron affinities of the cation A^+ and r_{A^+} and $r_{A^{\cdot}}$ denote the equilibrium geometries of the ion and radical respectively.

The majority of methods used to determine the EA for neutral species[48] are inapplicable to the determination of the EA for positive ions and the only way in which the latter can be found directly involves the study of the energy characteristics of the reverse process—the ionisation of the conjugate radicals:

$$A^{\cdot}(r_{A^{\cdot}}) \xrightarrow{IP_v(A^{\cdot})} A^+(r_{A^{\cdot}}) + e, \quad (7)$$

$$A^{\cdot}(r_{A^{\cdot}}) \xrightarrow{IP_{ad}(A^{\cdot})} A^+(r_{A^+}) + e, \quad (8)$$

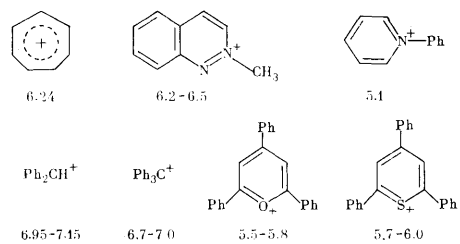
where $IP_v(A^{\cdot})$ and $IP_{ad}(A^{\cdot})$ are the vertical and adiabatic ionisation potentials of the conjugate radical $A^{\cdot}$.

Since only Eqns.(6) and (8) reflect the transition between identical energy levels, the determination of $IP_{ad}(A^{\cdot})$ makes it possible to determine simultaneously also $EA_{ad}(A^+)$, while the $IP_v(A^{\cdot})$ will in general differ from both $EA_v(A^+)$ and $EA_{ad}(A^+)$.

In view of the purely experimental difficulties in the determination of $IP(A^{\cdot})$, only a few ionisation potentials of radicals whose ionisation leads to cations forming stable CTC are at present known. One of these is the tropylium radical, whose $IP(A^{\cdot})$ is 6.24 eV [49,50] (obtained from Rydberg spectra). The electron impact method leads to a higher value (6.6 eV).[51] These differences can be largely caused by the method of measurement itself, since it is known that, without special modification of the measuring apparatus, the latter method yields unduly high results[52]. For benzene, whose values of IP_{ad} and IP_v are equal, the ionisation potential obtained by Tajima and Tsuchiya[52] is higher by 0.3 eV than the value of IP obtained from photoelectron spectroscopy. One must therefore assume that the true adiabatic ionisation potential of the tropylium radical is close to 6.24 eV. The ionisation potential of the N-methylcinnolinyl radical, amounting to 6.5 eV [53] (electron impact method), is also known. In the light of the foregoing, it is to be expected that the true ionisation potential of this radical is in the range 6.2–6.5 eV.

The photoelectron spectroscopic data mentioned by Kosower et al.[54], according to which the values of IP_v and IP_{ad} for the 1-ethyl-4-methoxycarbonylpyridyl radical are 7.2 and 6.8 eV respectively, must be regarded as erroneous. In all probability these ionisation potentials do not correspond to the ionisation of the pyridyl radical. The ionisation potential of the 1-phenylpyridyl radical, determined by the mass-spectrometric method and estimated from the IP of the corresponding 1,4-dihydropyridine, is 5.1 eV.[55] The IP for the triphenylmethyl radical can also be estimated approximately. According to the results of a study of the CTC of the diphenylmethyl and triphenylmethyl radicals with neutral π-acceptors[56], the value of IP for the latter is lower by ~0.2 eV. Assuming that the transition from the benzyl to the diphenylmethyl radical is associated with the same change in IP and using the value of IP_{ad} for the benzyl radical, which is 7.2–7.3 eV,[57,58] we find that IP_{ad} for the triphenylmethyl radical should be in the range 6.7–7.0 eV. Using mass-spectrometric data for pyrylium salts[59], one can estimate the IP also for the 2,4,6-triphenylpyrylium and 2,4,6-triphenylthiopyrylium radicals. Their values are most probably 5.5–5.8 and 5.7–6.0 eV respectively.

All the results described above make possible a direct estimate of the $EA(A^+)$ for acceptors which are listed below together with their structural formulae:



The results of quantum-chemical calculations also permit, in principle, the estimation of the EA for acceptor cations. The approximate nature of the versions of the calculations which are simplest in practice nevertheless makes it necessary to treat with caution the absolute values obtained, while the relative changes in the EA in individual series of compounds can be obtained with a fairly high accuracy.

At least three approaches can be used to calculate the EA. These involve the calculation of the $IP(A^{\cdot})$ and $EA(A^+)$ as the orbital energies in terms of the approximation of Koopmans theorem and the calculation of $EA(A^+)$ as the difference between the total energies of the radical and the ion. Calculation of the $IP(A^{\cdot})$ for tropyl, 1-methylpyridyl, 3-cyano-1-methylpyridyl, and 2-methoxycarbonyl-1-methylpyridyl radicals led to the following values: 8.85; 7.83; 7.96; and 8.73 eV respectively[60]. Despite the fact that all the results are much too high, the difference between the IP for tropyl and 1-methylpyridyl radicals agrees fairly well with experiment, which gives rise to hope for progress in this field when computational methods have been improved[61,62].

Calculations have been made in a number of studies for acceptor cations[63–67]. The most satisfactory agreement with the above experimental data has been obtained taking into account all the valence electrons. As an example, we shall present data obtained in the calculation for the N-methylpyridinium cation. According to the CNDO/2 method, the energy of the lowest vacant molecular orbital is 4.74 eV,[64] while a non-empirical calculation yielded[67] 5.23 eV.

The spectroscopy of the CTC and electrochemical reduction are indirect methods for the determination of the EA. According to Eqns.(3) and (4), the CT energy in both the

gas phase and in solution can be approximately expressed by the following relation:

$$h\nu_{CT} = IP(D) - EA(A^+) + E, \quad (9)$$

where E is a quantity which varies somewhat as a function of the conditions of the investigation. For known values of $h\nu_{CT}$, $IP(D)$, and $EA(A^+)$, it is possible to determine E and to estimate $EA(A^+)$ for other acceptor cations. This approach was first used by Feldman and Winstein[37], who established, on the basis of the results of a study of the CTC of the tropylium cation [$EA(A^+) = 6.24$ eV] that E in solution is close to 1.2 eV. This value agrees well with the expectation based on the analysis of the energy levels of the CTC of the given type, but differs markedly from that for the CTC between a neutral π-donor and a π-acceptor.

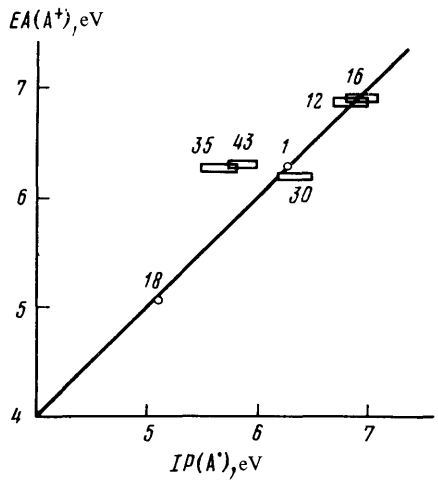


Figure 2. Dependence of the electron affinities of acceptor cations, determined by the method involving the study of CTC, on the ionisation potentials of the conjugate radicals. The points are numberd as in Table 3. In the case of the acceptor No.18 the value of $IP(A^·)$ for the N-phenylpyridyl radical was used; it is assumed that $IP(A^·)$ for acceptor No.16 is lower than $IP(A^·)$ for the diphenylmethyl radical (the difference may be 0.1–0.3 eV).

There is no reason to doubt that, in the study of different CTC under identical conditions, the value of E can be regarded as a constant to a satisfactory approximation under identical conditions in the vast majority of cases. The changes in E following the alteration of the solvent can be taken into account by studying a standard system (the CTC of the tropylium cation) in different solvents (Table 3).

It is noteworthy that certain complications arise because the CT band is associated with the vertical transition and the CT energy depends on $IP_v(D)$ and $EA_v(A^+)$. In this respect the parametrisation of Eqn.(5) relative to the EA_{ad} for the tropylium cation is justified only when $EA_v(A^+) = EA_{ad}(A^+)$ for this cation. Unfortunately measurements of the absolute values of these quantities have not been made for any acceptor cations and the increase in the complexity of the parametrisation produced by introducing any assumptions is at present unjustified. The satisfactory agreement between the values of $IP(A^·)$ and $EA(A^+)$ obtained by the method involving the study of the CTC (Fig.2) suggests that an equation of type (5) can be used to estimate $EA(A^+)$. Nevertheless one must bear in mind that the values of $EA(A^+)$ obtained in this way should vary in proportion to $EA_v(A^+)$ and can therefore differ from the values of $EA_{ad}(A^+)$ obtained by other methods. The difference should be particularly marked in the study of cations A^+ whose equilibrium geometry differs strongly from that of A (for example, arenediazonium salts).

Polarography is a second indirect method which is used fairly frequently to estimate EA.[48,76] It is most likely that the electrochemical reduction process carries information about the adiabatic addition of an electron and hence about the $EA_{ad}(A^+)$.

The half-wave potential for the reversible one electron reduction ($E_{1/2}$) can be expressed by the following equation with a satisfactory degree of approximation[77]:

$$E_{1/2} = EA + \Delta E_{solv} + Z, \quad (10)$$

where E_{solv} is the difference between the solvation energies of the reduced and oxidised forms and Z is a constant characterising the free energy of the electron in the standard electrode relative to that *in vacuo*.

The quantity ΔE_{solv} is virtually determined by the solvation energy of the charged species, since the solvation energies of neutral species are insignificant. The solvation energies of organic ions with a markedly delocalised charge in a series of polar solvents are ~2.0 eV [78] and vary comparatively little (by ±0.2 eV) when their structure is altered. The quantity Z for the saturated calomel electrode (s.c.e.) in acetonitrile solution is 4.38 eV.[78] When cations are reduced, the highly solvated species is the oxidised form and not the reduced form as happed in the reduction of neutral species. ΔE_{solv} therefore enters into Eqn.(10) with the opposite sign and $E_{1/2}$ in acetonitrile relative to the s.c.e. is expressed by the equation

$$E_{1/2}(V) = EA(A^+) - 6.38 \pm 0.2 \text{ (eV)}. \quad (11)$$

Using the literature data for the electrochemical reduction of acceptor cations[15,53,64,68,71,79–83], it is possible to test the validity of Eqn.(11). It follows from Eqn.(3) that in most cases there is an entirely satisfactory agreement between the $E_{1/2}$ and $EA(A^+)$. This agreement can actually be regarded as satisfactory, since the values of $E_{1/2}$ have been obtained in different solvents using different supporting electrolytes, which, together with the possible adsorption on the surface of mercury, can appreciably alter $E_{1/2}$.[84,85]

The data for acceptors Nos.41, 44–46, and 49 deviate from the overall relation (Fig.3). Whereas in the case of dibenzopyrylium (No.41) this can be associated with inaccurate experimental data, for benzenediazonium acceptor cations[40] the problem can be complicated by the appreciable difference between $EA_v(A^+)$ and $EA_{ad}(A^+)$. In this case one can assume that the experimental $EA(A^+$, CTC) are insufficiently high for Eqn.(11) to be observed and that the deviations of the experimental points vary with the substituent. Since this does actually occur, presumably the difference between $EA_{ad}(A^+)$ and $EA_v(A^+)$ for benzenediazonium ions reaches ~1 eV. For heteroaromatic and also carbonium ions, there is no reason to believe that the difference between the adiabatic and vertical electron affinities exceeds 0.2–0.3 eV. It should also be assumed that the parametrisation of Eqn.(5) has been carried out correctly and that the data in Table 3 reflect the true vertical values of EA for acceptor cations, which, with the exception of hetero-onium ions, are close to the adiabatic values.

Table 3. The CT energies and the values of $EA(A^+)$ obtained on their basis.

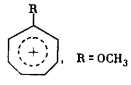
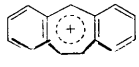
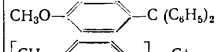
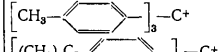
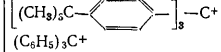
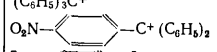
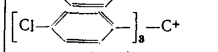
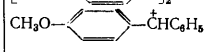
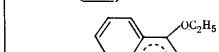
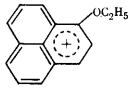
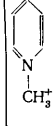
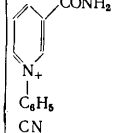
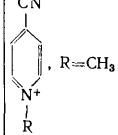
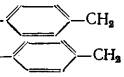
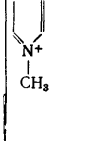
No.	Acceptor	Donor*	Solvent	λ_{max}, nm	$h\nu$, eV	Refs.	IP(D), eV	E_{11}, eV	$EA(A^+)$, eV
1		perylene	CH_2Cl_2	611	2.03	[27]	7.12	1.15	6.24
	ditto	anthracene	CH_2Cl_2	535	2.32	[27,41]	7.4	1.16	—
	»	pyrene	CH_2Cl_2	535	2.32	[41,42,68]	7.53	1.03	—
	»	HMB	CH_2Cl_2	437	2.87	[27,41]	7.95	1.16	—
	»	phenanthrene	CH_2Cl_2	428	2.90	[27]	8.03	1.11	—
	»	anthracene	CH_3CN	488	2.54	[37]	7.4	1.35	—
	»	pyrene	CH_3CN	488	2.54	[42]	7.54	1.25	—
	»	HMB	CH_3CN	417	2.98	[24,37]	7.95	1.27	—
	»	naphthalene	CH_3CN	398	3.11	[37]	8.12	1.23	—
	»	NDMA	$CH_2Cl_2 : CH_3CN = 1 : 1$	571	2.17	[69]	7.45	0.96	—
2		pyrene	CH_2Cl_2	480	2.59	[68]	7.53	1.05**	6.0
3	ditto , R=OH	pyrene	CH_2Cl_2	450	2.76	[68]	7.53	1.05	5.8
4	» , $R=C(CH_3)_3$	pyrene	CH_2Cl_2	503	2.47	[68]	7.53	1.05	6.1
5	» , R=Br	pyrene	CH_2Cl_2	585	2.12	[68]	7.53	1.05	6.5
6	» , R=Cl	pyrene	CH_2Cl_2	605	2.05	[68]	7.53	1.05	6.55
7	» , R=CN	pyrene	CH_2Cl_2	680	1.83	[68]	7.53	1.05	6.75
8		durene	CH_2Cl_2	447	2.78	[37]	8.3	1.18	6.7
	ditto	HMB	CH_2Cl_2	522	2.38	[37]	7.95	1.13	—
	»	pyrene	CH_2Cl_2	667	1.86	[37]	7.53	1.05	—
9		pyrene	CH_2Cl_2	575	2.26	[68]	7.53	1.05	6.4
10		pyrene	CH_2Cl_2	640	1.94	[68]	7.53	1.05	6.65
11		pyrene	CH_2Cl_2	705	1.76	[68]	7.53	1.05	6.8
12		pyrene	CH_2Cl_2	710	1.75	[68]	7.53	1.05	6.85
13		pyrene	CH_2Cl_2	790	1.57	[68]	7.53	1.05	7.0
14		pyrene	CH_2Cl_2	820	1.51	[68]	7.53	1.05	7.05
15		pyrene	CH_2Cl_2	675	1.84	[68]	7.53	1.05	6.75
16		pyrene	CH_2Cl_2	725	1.71	[68]	7.53	1.05	6.85
17		pyrene	CH_2Cl_2	674	1.84	[37]	7.53	1.05	6.75
	ditto	anthracene	CH_2Cl_2	713	1.74	[37]	7.40	1.05	—
18		TMPD	$CHCl_3$+5% C_2H_5OH	430	2.88	[23]	6.75	1.2	5.05
19		anthracene	dioxan : water = 6 : 4	391	3.17	[70]	7.40	1.25	5.5
20	 , R=CH_3	NDMA	C_2H_5OH (96%)	433	2.86	[29]	7.45	1.25	5.85
	ditto , R=CH_3	TMOB	C_2H_5OH (96%)	473	2.62	[29]	7.20	1.25	—
	» , R=CH_3	pyrene	$CHCl_3$+5% C_2H_5OH	434	2.86	[38]	7.20	1.25	5.85
21	» , R=n-C_4H_9	TMOB	C_2H_5OH (96%)	473	2.62	[29]	7.20	1.25	5.85
22	» , R=O_2N- 	TMOB	C_2H_5OH (96%)	486	2.55	[29]	7.20	1.25	5.9
23	» , R=CHO_3-	TMOB	C_2H_5OH (96%)	482	2.57	[29]	7.20	1.25	5.9
24		NDMA	C_2H_5OH (96%)	430	2.89	[29]	7.45	1.25	5.8

Table 3 (contd.).

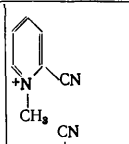
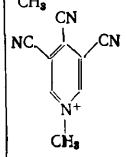
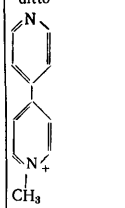
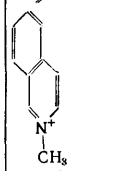
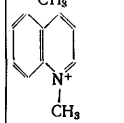
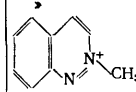
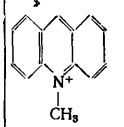
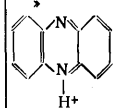
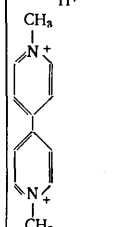
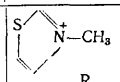
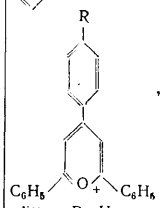
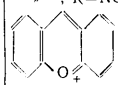
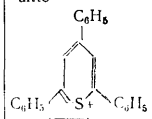
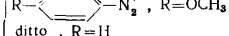
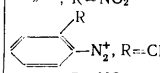
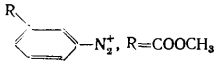
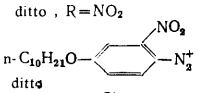
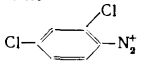
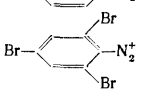
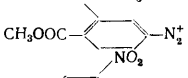
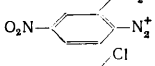
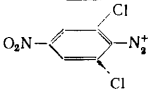
No.	Acceptor	Donor*	Solvent	λ_{max}, nm	$h\nu$, eV	Refs.	$IP(D)$, eV	E_{11}, eV	$EA(A^+)$, eV
25		NDMA	C_2H_5OH (96%)	478	2.59	[71]	7.45	1.25	6.1
26		HMB	CH_2Cl_2	507	2.45	[37]	7.95	1.1	6.6
	ditto	pyrene	CH_2Cl_2	620	2.0	[37]	7.53	1.05	—
27		naphthalene	$CHCl_3$+10% C_2H_5OH	338	3.67	[38]	8.12	1.2	5.65
	ditto	pyrene	$CHCl_3$+10% C_2H_5OH	400	3.1	[38]	7.53	—	—
	»	anthracene	$CHCl_3$+10% C_2H_5OH	416	2.98	[38]	7.40	—	—
28		TMDP	$CHCl_3$+5% C_2H_5OH	500	2.48	[23]	6.75	1.2	5.45
29		NDMA	$C_2H_4Cl_2$	430	2.88	[72]	7.45	1.05	5.6
	ditto	anthracene	$CHCl_3$+5% C_2H_5OH	415	2.72	[22]	7.12	1.2	—
	»	perylene	$CHCl_3$+5% C_2H_5OH	456	2.72	[22]	7.12	1.2	—
	»	pyrene	$CHCl_3$+5% C_2H_5OH	420	2.95	[73]	7.53	1.2	—
30		naphthalene	$CHCl_3$+5% C_2H_5OH	403	3.08	[38]	8.12	1.2	6.2
	ditto	pyrene	$CHCl_3$+5% C_2H_5OH	496	2.5	[38]	7.53	1.2	—
	ditto	anthracene	$CHCl_3$+5% C_2H_5OH	508	2.44	[38]	7.4	1.2	—
	»	perylene	$CHCl_3$+5% C_2H_5OH	564	2.20	[38]	7.12	1.2	—
31		pyrene	CH_2Cl_2	505	2.46	[42]	7.53	1.05	6.15
	ditto	anthracene	CH_2Cl_2	517—525	2.36—2.40	[30,37]	7.40	1.05	—
	»	perylene	CH_2Cl_2	595	2.09	[30,37]	7.12	1.15	—
	»	anthracene	$CHCl_3$	508	2.44	[41]	7.4	1.20	—
	»	NDMA	CH_2Cl_2	538	2.3	[69]	7.45	1.05	—
	»	NDMA	$C_2H_4Cl_2$	560	2.21	[72]	7.45	1.05	—
32		pyrene	CH_3CN	620	2.0	[74]	7.53	1.25	6.8
33		pyrene	CH_3OH	468	2.65	[31]	7.53	1.25	6.15
	ditto	perylene	CH_3OH	531	2.34	[31]	7.12	1.25	—
	»	naphthalene	CH_3OH	383	3.24	[31]	8.12	1.25	—

Table 3 (contd.).

No.	Acceptor	Donor*	Solvent	λ_{max}, nm	$h\nu$, eV	Refs.	$IP(D)$, eV	E_{II}, eV	$EA(A^+)$, eV
34		2,6-dimethylnaphthalene	CH_3CN	280	4.43	[23]	7.82	1.25	4.6
35	 , R=H	DMPD	CH_3CN	360	3.45	—	6.75	1.25	—
	ditto , R=H	anthracene	CH_2Cl_2	570	2.18	[15]	7.4	1.05	6.3
36	» , R=OCH_3	anthracene	CH_2Cl_2	540	2.27	[15]	7.4	1.05	6.2
37	» , R=Cl	anthracene	CH_2Cl_2	580	2.14	[15]	7.4	1.05	6.3
38	» , R=$COOCH_3$	anthracene	CH_2Cl_2	600	2.01	[15]	7.4	1.05	6.4
39	» , R=CN	anthracene	CH_2Cl_2	610	2.03	[15]	7.4	1.05	6.4
40	» , R=NO_2	anthracene	CH_2Cl_2	610	2.03	[15]	7.4	1.05	6.4
41		pyrene	CH_2Cl_2	660	1.88	[68]	7.53	1.05	6.7
42		isobutene	CH_3CN	400	3.1	[75]	9.35	1.25	7.5
	ditto	cyclohexene	CH_3CN	434	2.86	[75]	9.12	—	—
43		anthracene	CH_2Cl_2	580	2.14	[15]	7.40	1.05	6.3
44	 , R=OCH_3	pyrene	CH_3NO_2	365	3.4	[40]	7.53	1.25	5.4
45	ditto , R=H	pyrene	CH_3NO_2	420	2.95	[40]	7.53	1.25	5.85
	» , R=H	2,6-dimethylnaphthalene	CH_3NO_2	385	3.22	[40]	7.82	1.25	—
46	» , R=Br	pyrene	CH_3NO_2	450	2.76	[40]	7.53	1.25	6.0
47	» , R=Cl	pyrene	CH_3NO_2	445	2.79	[40]	7.53	1.25	5.95
48	» , R=$COOC_2H_5$	pyrene	CH_3NO_2	485	2.56	[40]	7.53	1.25	6.2
49	» , R=NO_2	pyrene	CH_3NO_2	540	2.30	[40]	7.53	1.25	6.5
50	 , R=Cl	pyrene	CH_3NO_2	490	2.53	[40]	7.53	1.25	6.25
51	ditto , R=NO_2	pyrene	CH_3NO_2	572	2.17	[40]	7.53	1.25	6.6
52	 , R=$COOCH_3$	pyrene	CH_3NO_2	485	2.56	[39,40]	7.53	1.25	6.15
53	ditto , R=NO_2	pyrene	CH_3NO_2	510	2.43	[39,40]	7.53	1.25	6.4
54		pyrene	$CHCl_3$	544	2.28	[34]	7.53	1.10	6.3
	ditto	anthracene	$CHCl_3$	554	2.24	[34]	7.40	—	—
55		pyrene	CH_3NO_2	500	2.48	[39]	7.53	1.25	6.3
56		pyrene	CH_3NO_2	520	2.38	[39]	7.53	1.25	6.4
57		pyrene	CH_3NO_2	520	2.38	[39]	7.53	1.25	6.4
58		anthracene	CH_3NO_2	753	1.65	[39]	7.40	1.25	7.0
59		pyrene	CH_3NO_2	695	1,78	[39]	7,40	1,25	7,0

*Notation: HMB = hexamethylbenzene; NDMA = *N*,*N*-dimethylaniline; TMPD = *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine; TMOB = 1,2,3,5-tetramethoxybenzene.

**Here and henceforth the values of E_{II} have been adopted on the basis of the results for the CTC of the tropylium cation and the average value of $EA(A^+)$ has been rounded off to 0.05 eV.

Despite the limited number of studies whose results permit a direct estimation of the absolute values of $EA(A^+)$ in the gas phase, there is no doubt that the latter greatly exceed the values for neutral electron acceptors[48]. For example, *EA* for one of the weakest acceptor cations (*N*-methylpyridinium) is ~5.05 eV, while *EA* for one of the strongest neutral electron acceptors (tetracyanoquinodimethane) is ~2.8 eV. On the other hand, if one considers the entire set of possible acceptors, one may conclude that the CTC with clearly detectable CT bands are formed by neutral acceptors whose *EA* are in the range 0.5–3.0 eV and acceptor cations for which the *EA* are 4.5–7.0 eV. In fact these limits of the *EA* lie in both cases in an intermediate region between the values reflecting a weak CTC type interaction and those characteristic of one-electron transfer. Therefore another conclusion is also valid, namely in a condensed phase a neutral acceptor and an acceptor cation manifest approximately the same electron-accepting properties, provided that the *EA* (in the gas phase) for the latter exceeds ~4 eV. This difference is due to the effects of solvation or polarisation of the medium, which are clearly shown on comparing the photoelectron spectra of solutions and gases comprising neutral substances and ions[85–87]. The external ionisation potential for solutions of neutral molecules is lower by 1–2 eV and for solutions of ions is higher by 2–3 eV than the corresponding characteristics in the gas phase[88]. On this basis, we arrive at the analogous conclusion that a neutral molecule and an ion have approximately the same electron-donating or electron-accepting properties in solution, provided that their values of *IP* and *EA* in the gas phase differ on average by 4 eV.

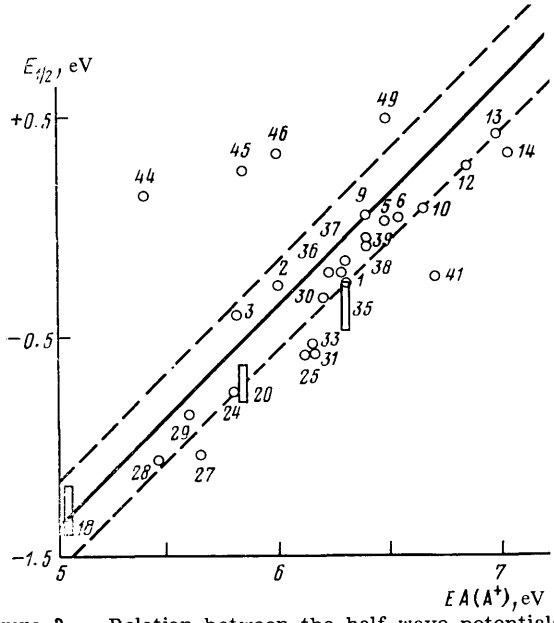


Figure 3. Relation between the half-wave potentials of the polarographic reduction of A^+ and $EA(A^+)$ obtained from the study of CTC. The acceptors are numbered as in Table 3. The straight lines have been drawn on the basis of Eqn.(11).

V. THE PHOTOCHEMICAL PROPERTIES OF THE CHARGE-TRANSFER COMPLEXES OF ARENEDIAZONIUM IONS

The ability of arenediazonium ions to decompose under the influence of light constitutes the basis of many non-silver photographic materials and photoresistors[20,21,89–93]. Many of these contain a substituted benzenediazonium cation as the light-sensitive substance. As a rule, a disadvantage of these materials is a comparatively low overall and not especially favourable spectral sensitivity. On formation of CTC with neutral π-donors, new absorption bands appear, which in principle can lead to the expansion of the spectral sensitivity and an increase of the overall light sensitivity of such materials[20,21,94]. Indeed, depending on the donor and arenediazonium salt employed, CT bands can occur up to 750 nm (see Table 3) which, in the case of photodecomposition on irradiation with light corresponding to the given band, should naturally lead to an appreciable expansion of spectral sensitivity. The photodecomposition on irradiation with light corresponding to the CT band can be regarded as a special case of the familiar radical mechanism of photodecomposition[20,21,95]. In the general case benzenediazonium salts can decompose via both ionic and radical mechanisms[20,21,94], which in isolated instances can be complicated by other processes[96]:

$$ArN_2^+ \longrightarrow N_2 + Ar^+ \xrightarrow{R^1OH} ArOR^1$$

$$ArN_2^+ \longrightarrow ArN_2^{\cdot} \rightarrow Ar^{\cdot} + N_2 \xrightarrow{R^2R^3CHOH} \rightarrow ArH + R^2R^3\dot{C}{-}OH \xrightarrow{ArN_2^+} \text{chain propagation.}$$

Photodecomposition via an ionic mechanism can be regarded as a consequence of intramolecular electron transfer to the diazonium group and leads to nucleophilic substitution products. This pathway cannot be achieved with a quantum yield ϕ exceeding unity. Photodecomposition via a radical mechanism can be regarded as a consequence of intermolecular electron transfer and leads to reduction products. Despite the fact that in the given instance the primary photoprocess cannot be achieved with $\phi > 1$, the overall quantum yield can exceed unity owing to the occurrence of chain reactions with participation of the solvent or the polymer matrix[21,34,97–100]. For example, in alcoholic solutions chain propagation can proceed via the following mechanism:

$$ArN_2^+ + R_2\dot{C}{-}OH \rightarrow ArN_2^{\cdot} + R_2C{=}O + H^+,$$

$$ArN_2^{\cdot} \rightarrow Ar^{\cdot} + N_2 .$$

The solvent, the corresponding anion, or a neutral electron donor can serve as a source of the external electron necessary for the first stage[21,34]. This process is limited thermodynamically by the energy necessary for electron transfer and the free energy of activation is expressed by the following equation[21,34]:

$$\Delta G^{\neq} = E_{1/2}^{oxy}(D) - h\nu_{00} - E_{1/2}^{red}(A^+),$$

where $E_{1/2}^{oxy}(D)$ is the half-wave potential for the anodic oxidation of the donor and $h\nu_{00}$ is the energy of the 0–0 transition on excitation of the donor, acceptor, or the CTC (for a thermal process, $h\nu_{00} = 0$).

Simple ideas about orbital symmetry in photochemical reactions confirm the occurrence of the adiabatic transition from the excited CT state to the aryldiazo-radical[101] and the experimental results for solutions[21,34,94,100,101] demonstrate the validity of the ideas described above. Irradiation with

light corresponding to the CT band leads to the decomposition of the arenediazonium ion[34] and the photolysis of the CTC of the *p*-chlorobenzenediazonium ion with pyrene results in 100% formation of chlorobenzene. An analogous increase of the amount of the products of the photodecomposition via the radical mechanism has been observed also in other instances[34, 100,101]. The operation of the radical mechanism is also indicated by the influence of various inhibitors of similar reactions on the process[34,100,101].

The quantum yield of the photodecomposition by light corresponding to the CT band depends on a number of factors[34]. It increase on enhancement of the electron-donating, properties of the donor D and the electron-accepting properties of the acceptor A^+ and with increase of the concentration of the H-donor solvent and diminishes in the presence of oxygen and other radical traps and also with increase of the donor concentration. When the CTC of pyrene with the 4-chlorobenzenediazonium ion was irradiated with light at $\lambda = 405$ nm in an atmosphere of nitrogen in a mixed solvent (dioxan : acetonitrile = 4 : 1), the yield ϕ exceeded 10 for certain concentration ratios[34]. In an atmosphere of oxygen the quantum yield of the photodecomposition was ~0.1.

Consequently, despite the fact that the use of CTC of arenediazonium ions with neutral electron donors does in principle make it possible to eliminate the significant disadvantages of the photographic materials based on diazonium salts used nowadays, their practical application constitutes an extremely complex problem. In a polymer matrix it is complicated still further by the restriction of diffusion which prevents the release of the primary radical pair from the cage.

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Influence of Ring Size on Properties and Reactivity of Cyclic Systems

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Results obtained during 1960-1979 on the effect of the size of a saturated or partly hydrogenated carbo- or hetero-cycle on the physicochemical (spectral, polarographic, ionisation) and chemical properties of cyclic compounds are summarised. Attention is paid mainly to the usual (C_5-C_7) cyclic systems. Results are interpreted in terms of classical strain theory, the *I*-strain concept, and the Finnegan-Streitwieser rehybridisation model. A list of 173 references is included.

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I. INTRODUCTION

The influence of the size of a saturated or partly hydrogenated ring on the properties and the reactivity of a cyclic system is now well known and continually subject to close attention by organic chemists. This problem is dealt with in some way or another in all the many monographs and reviews[1-10] concerned with aspects of the stereochemistry of cyclic compounds. However, the ever increasing information on this topic has not been subjected to detailed analysis since publication of the 1960 review[9]. The present survey is intended in some measure to fill this gap. Nevertheless, it is not possible to cover all aspects of the problem, and this Review will be confined mainly to the "usual" (C_5-C_7) and to a less extent small (C_3, C_4) rings. Information on rings larger than seven-membered has not been specially systematised (reviews have appeared[11,12]), and is considered only when necessary to ensure completeness of exposition.

Although the data given below are largely determined by the strain in the rings, it seems useful to include appropriate thermodynamic parameters, which have been summarised in detail in the above monographs and reviews[1-3,9]. Results published during recent years[13-15] do not change fundamentally existing information on the relative stabilities of cyclic systems. It must be noted only that the strain sequence known for carbocyclic derivatives is on the whole maintained in saturated heterocyclic compounds[15].

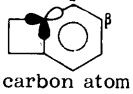
The premises on which experimental results obtained to establish a correlation between properties and ring size can be interpreted have now been quite well developed. They involve primarily the types of strain inherent in the systems† and the changes they undergo on passing from the ground to the transition state (or final state in the case of equilibrium).

† These comprise mainly Baeyer or angular strain involving distortion of bond angles; Pitzer or torsional strain, due to the "striving" of substitutents attached to adjacent atoms to avoid an unfavourable eclipsed conformation and to occupy the energetically most favourable relative positions; transannular interaction (across the ring); *F*-strain, i.e. increase in steric strain on formation of a bond between two atoms, due to spatial interaction of substituents attached to these atoms; and finally *I*-strain—change in the internal strain of the cyclic system due to changes in angles and conformation accompanying change in the coordination number of a ring atom during reaction[9].

An important supplement to such a treatment, especially in connection with the concept of *I*-strain, is that differences in reactivity between compounds depending on ring size are determined, under otherwise similar conditions, also by how far along the reaction coordinate the transition state was formed (i.e. whether the latter was "initial-like" or "final-like"). If achievement of the transition state involves rehybridisation of a ring atom, the influence of ring size will be considerably less marked in the former than in the latter case[16].

Even the most rigorous examination possible of all types of strain and their variation during a reaction in no way exhausts all aspects of the problem and relates mostly to reactions involving a ring atom. Simple angular strain clearly cannot provide an interpretation of the overall effect of a fused ring on the reactive behaviour of a molecule, e.g. the Mills-Nixon effect. Results on effects of this type were generalised[17,18] with an explanation that has now been confirmed by many spectral and kinetic investigations[19,20].

According to this generalisation aryl positions attached to a strained fused ring (α-positions) exhibit diminished reactivity towards electrophilic reagents. The reason is enhancement of the *p*-character of those orbitals (shown solid)



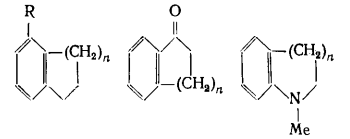
that are directed from a carbon atom of the benzene ring towards the strained ring with consequent enhancement of the *s*-character of the orbitals (shown open) directed towards the α-position of the benzene ring. Such increase in *s*-character clearly improves the electron-accepting properties of the orbital and hence lowers the reactivity of the α-position towards electrophilic reagents with greater acidity of the corresponding carbon-hydrogen bonds. These conditions provide a good explanation of the Mills-Nixon effect[21], i.e. why in indane derivatives (which contain a strained five-membered ring), in contrast to tetrahydronaphthalene derivatives, electrophilic substitution is oriented predominantly at a β-position.

II. PHYSICOCHEMICAL PROPERTIES OF CYCLIC SYSTEMS

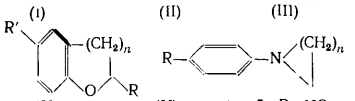
1. Spectral Properties

Spectral methods, in particular electron spectroscopy, have been widely used to elucidate reasons for the differences in reactivity between cyclic systems varying in ring

size. Mention must first be made of several early papers on bicyclic derivatives, not covered in existing reviews. Examination of the ultraviolet spectra of benzocycloalkanes (I),[22] benzocycloalkanones (II),[23] and heterobicyclic compounds (III) and (IV)[24–26] indicated that maximum conjugation was present in the almost planar five-membered ring:



(I) (II) (III)



(IV) (V): $n = 1-5$, R=NO_2; (VI): $n = 1-4$, R=H

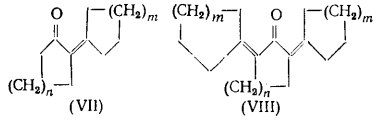
Study of the ultraviolet spectra of the *N*-arylazacycloalkanes (V) and (VI) has revealed[27] for the aziridine derivative (V: $n = 1$) a strong hypsochromic displacement of the absorption maximum and a decrease in the extinction coefficient relative to the other compounds of this series. Some fall in intensity and shift in the absorption maximum to shorter wavelengths is observed also with the *N*-arylpiperidine (V: $n = 4$). The conclusion[27] that sp^3-hybridisation of the nitrogen atom occurs in the former compound and inhibition of conjugation in the latter, six-membered compound is confirmed by the nuclear magnetic resonance spectra (down-field shift in the signals from *ortho*-protons of the benzene ring) and by measurements of the ionisation constants (subsection 2).

Other workers[28] who studied the ultraviolet spectra of *N*-phenylazacycloalkanes (VI: $n = 1-4$) assumed that the nitrogen atom has an sp^3-configuration in all the compounds, but the degree of conjugation decreases according to ring size in the sequence

$$C_5 > C_4 > NN\text{-dimethylaniline} > C_6 > C_3$$

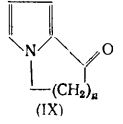
which is consistent with the exaltation of molecular refraction. In this case the degree of conjugation is determined by the angle ϕ between the direction of the orbital bearing the lone pair of electrons of the nitrogen atom and the normal to the plane of the benzene ring, with increase in ϕ leading to a weakening of absorption. From an analysis of molecular models it was concluded[28] that for a five-membered ring $\phi = 0$, whereas for a six-membered ring $\phi > 0$ owing to interaction of α-protons of the piperidine ring with *ortho*-protons of the benzene ring.

A study[29] of the electronic spectra of the cycloalkylidene ketones



(VII) (VIII)

also showed that five-membered compounds absorb in the ultraviolet at longer wavelengths than do six-membered compounds. Analysis of the spectra of the fused pyrroles



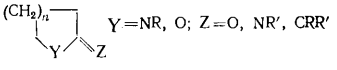
(IX)

($n = 1-3$) also indicated[30] that conjugation of the carbonyl with the pyrrole ring is best in the five-membered compound ($n = 1$). The infrared spectra of the pyrroles (IX) were also examined, and found to be closely similar for the six- and seven-membered compounds (ν_{CO} respectively 1650 and 1645 cm^{-1}) but appreciably different for five-membered compounds (1700 cm^{-1}). The increase in the carbonyl frequency in the spectrum of (IX: $n = 1$) was attributed[30] to enhancement of the *s*-character of the orbital directed towards the oxygen atom.

Analogous results were obtained from the infrared spectra of cycloalkanones, lactams, lactones, cyclic ureas, imides, urethanes, and other compounds of similar type[31]. The carbonyl frequencies were regarded[31] in all cases as indicating not ring-strain by hybridisation of the orbital directed towards the oxygen atom: enchancement of the *s*-character of this orbital, which increases on passing from seven- and six-membered to five- and four-membered rings, is the reason for the higher ν_{CO} frequency in compounds having strained rings.

Hypotheses of this type are consistent with a very good correlation[32] between the acetolysis rate constants of toluene-*p*-sulphonates $RR'CHOSO_2Ar$ and the carbonyl frequencies of the corresponding ketones. From this it can be concluded that the two parameters are equally sensitive to angular strain and to hybridisation. The correlation does not apply to compounds whose hydrolysis is sterically accelerated, as e.g. the pair cyclopentyl toluene-*p*-sulphonate and cyclopentanone.

The above views on the correlation between carbonyl frequency and the *s*-character of the hybride orbital are apparently quite valid for non-conjugated systems[33]. For systems in which the carbonyl is conjugated with other groups Y, as in lactams, lactones, etc.

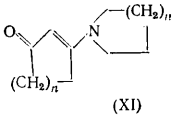


Y=NR, O; Z=O, NR', CRR'

(this applies also to other types of compounds having a conjugated exocyclic double bond—enamines and amidines), however, it must also be borne in mind that such conjugation is best realised in a six-membered ring[34,35], and the increase in the carbonyl (or C : C or C : N) frequency for five-membered compounds must be partly attributed to inhibition of conjugation in them#.

Enhancement of the *s*-character of the C–O orbital in strained cycloalkanones affects also their capacity for hydrogen bonding (determined from the infrared spectra). Depending on ring size the strength of the hydrogen bond diminishes in the sequence $C_5 < C_6 < C_7$.[37] For cyclic imines[38] and ethers[39] it has been shown earlier that hydrogen bonding is stronger in five- than in six-membered compounds. For lactones[39], on the other hand, the situation is similar to that observed for cyclic ketones, and valerolactone forms a stronger hydrogen bond with methanol than does butyrolactone. Comparison of the behaviour of lactones and cyclic ethers indicated[30] that in the former the carbonyl oxygen is involved in hydrogen bonding.

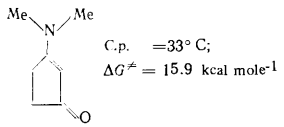
Several comparisons have been made of ^1H n.m.r. spectra as a function of ring size[40–42]. The chemical shifts of signals from vinyl protons of enamines, e.g. of type



(XI)

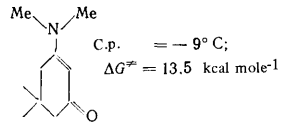
The increase in carbonyl frequency in five-membered rings in a series of benzolactams has been explained in terms of diminished conjugation between carbonyl and imino-groups[36].

indicate that delocalisation of the electron pair of the nitrogen atom is more strongly marked in five- than in six-membered compounds[40,41]. These results are confirmed by infrared and ultraviolet spectra and also by the greater restriction of rotation about the carbon–nitrogen bond in the five-membered enamino-ketone (XII) than in its six-membered analogue (XIII)§:



C.p. =33° C;
$\Delta G^{\neq} = 15.9$ kcal mole^{-1}

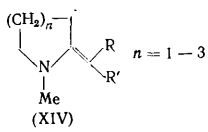
(XII)



C.p. = — 9° C;
$\Delta G^{\neq} = 13.5$ kcal mole^{-1}

(XIII)

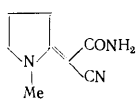
In a detailed analysis of the influence of ring size on the barrier to rotation about the carbon–carbon double bond in enamines of the type



$n = 1 - 3$

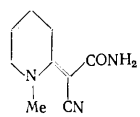
(XIV)

it was established[42] by ^{1}H n.m.r. spectroscopy that restricted rotation occurs with a comparatively low energy barrier, with activation free energies of *cis–trans* isomerisation lowest for six-membered and highest for five-membered compounds. A characteristic example is[42]



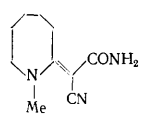
C.p. °C 71°

$\Delta G^{\neq}$ kcal mole^{-1} 19.1; 17.4



—14°

13.1; 13.7

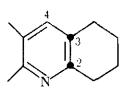


45°

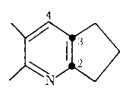
16.0; 16.3

Interpretation of these results was based on the conclusion that the energy of the transition state is significantly higher for five- than for six-membered compounds owing to the unsuitability for the former of transformation of the exocyclic into an endocyclic double bond.

Annelated pyridines have recently been studied[20] by ^{13}C n.m.r. spectroscopy. On passing from six-membered (XV) to five-membered (XVI) analogues



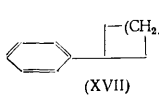
(XV)



(XVI)

the signals from carbon atoms 2 and 3 undergo down-field shifts of ~8–9 and 4.8–5 ppm respectively, which agrees well with the stronger electron-accepting effect of a strained five-membered ring (Section I). Thus annelation with a strained ring enhances the electronegativity of the nitrogen atom and carbon atom 4, with consequent deshielding of the carbon atoms at positions 2 and 3.

Study of the fragmentation under electron bombardment of the compounds



(XVII)

n	1	2	3
E_a, kcal mole^{-1}	34.5±4.8	53.5±4.8	62.5±4.8

has established[43] a parallelism between stability of the ring and resistance to electron impact: i.e. the activation energy of fragmentation E_a increases on passing from the strained cyclobutane and cyclopentane rings to the unstrained cyclohexane ring.

2. Ionisation Constants

Most research on the dependence of physicochemical properties on ring size has been based on the measurement of ionisation constants and interpretation of the results[44–73]. Firstly we must note that the kinetic acidity of cycloalkanes varies[44] in the sequence¶

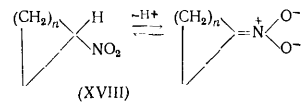
$$C_3 \gg C_4 > C_5 > C_6 \approx C_9 > C_7 \approx C_{10} > C_8 \approx C_{11} > C_{12} > C_{14}.$$

The divergence of these results from those for the rates of solvolysis of the corresponding toluene-*p*-sulphonates led to the conclusion[44] that the conformations of initial and final states (cycloalkane and cycloalkyl anion) are closely similar, and the differences in acidity are determined solely by the degree of *s*-character of the C–H orbital. These workers[44] regarded this conclusion as supported by the good correlation of kinetic acidities with the $J(^{13}C–H)$ values characterising hybridisation.

The action of n-butylsodium on mixtures of cyclopentene and cyclohexene showed[46] that the carbon–hydrogen bond in the former cycloalkene possesses the more acidic properties. On the other hand, measurement of the basicity of unsaturated ketones —cyclopent-2-enone and cyclohex-2-enone—revealed no effect of ring size[47]. The acidity of a series of nitrocycloalkanes

$$C_8 > C_7 > C_5 > C_6 > C_4 \gg C_3$$

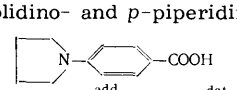
diminishes with ring size in the sequence[48]



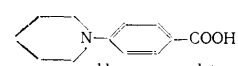
(XVIII)

The greater acidity of seven- and five-membered than of six-membered compounds agrees well with the change from sp^3 to sp^2 hybridisation of the cyclic carbon atom accompanying formation of an anion, i.e. with the concept of *I*-strain.

Considerably more research in this field has been done on heterocyclic compounds. It has been shown[27] for *N*-aryl-azacycloalkanes that five-membered compounds are least basic, which is due to steric inhibition of conjugation of the nitrogen lone pair with the benzene ring (subsection 1)†. Basicity and acidity constants had been determined[50] for *p*-pyrrolidino- and *p*-piperidino-benzoic acids:



(XIX), $pK_a^{add} = 0.39$; $pK_a^{det} = 6.07$



(XX), $pK_a^{add} = 2.67$; $pK_a^{det} = 5.75$

where pK_a^{add} and pK_a^{det} correspond to addition and detachment of a proton respectively. Comparison with the acidity constants of corresponding acyclic compounds (e.g. for *p*-dimethylaminobenzoic acid (XXI) $pK_a^{det} = 6.0$) shows[50] that (XX) is characterised by considerable steric inhibition

§ Here and subsequently C.p. = coalescence temperature (point).

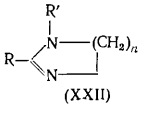
¶ Different relations apparently occur among chlorofluoroalkenes[45].

† Similar results had been obtained earlier for *N*-phenylpyrrolidine and -piperidine[49].

of resonance interaction, due to overlapping of the orbitals of α-protons of the piperidine ring with those of *o*-protons of the benzene ring.

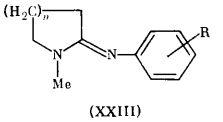
The very low basicity of (XIX) in comparison with not only (XX) but also (XXI) ($pK_a^{det} = 1.40$) was attributed[50] to non-bonded interactions occurring on protonation of the pyrrolidine nitrogen atom, accompanied by a change in its configuration from sp^2 to sp^3. The Reviewer regards such an explanation as entirely logical; from these results the hypothesis of an sp^3 configuration for the nitrogen atom in all *N*-phenylazacycloalkanes (subsection 1) can be considered improbable. Basicity measurements on oxacycloalkanes[51] gave the same sequence depending on ring size $C_5 > C_7 > C_6$ as for cyclic imines#. The effect of *F*-strain during protonation was regarded as insignificant (application of this concept would have given the different sequence $C_5 > C_6 > C_7$), and the results were explained in terms of the so called electronic correlation effect. This explanation presupposes that repulsion of the lone pair of the oxygen atom from the α–C–H group accompanying protonation at the oxygen would be more greatly diminished for five- and seven-membered rings (where shielding is present) than for a six-membered ring. It was supposed that this would relieve a certain proportion of the strain on the protonation of oxygen in a five-membered (and to a less extent seven-membered) ring. Since shielding is absent from a six-membered ring, this effect plays no part; hence an additional gain in energy accompanies protonation of five- and seven-membered compounds, so that they are more basic than the pyran derivative.

Among cyclic amidines



(XXII)

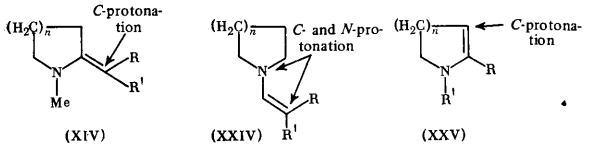
the most basic are hydrogenated pyrimidine derivatives, which are followed by seven- and eight-membered compounds, the least basic being imidazolines (XXII: $n = 1$).[53] The same sequence $C_6 > C_7 > C_5$ is maintained[35] in amidines of the different type



(XXIII)

The explanation of such variation in basicity is that the best conditions for conjugation of the lone pair of the cyclic nitrogen atom with the exocyclic double bond occur in the six-membered ring§. Correlation analysis showed[35] that rotation of the benzene ring relative to the plane of the C : N bond depends little on ring size.

Several studies have been made of the basicity of tertiary enamines

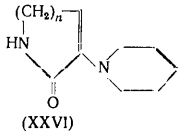


(XIV) (XXIV) (XXV)

The same sequence had previously been obtained[52] for cyclic ethers, but a different sequence for lactones ($C_6 > C_5 > C_4$) and cycloalkanones ($C_7 > C_6 > C_5 > C_4$), which indicates a change in the site of protonation (at the carbonyl oxygen) for these compounds.

§ Such an explanation had earlier been advanced[34] in connection with the basicity of lactams.

For the compounds of type (XIV) the sequence $C_6 > C_7 > C_5$ has been established[54–56] for the variation of basicity with ring size¶. Study of restricted rotation about ethylenic bonds in these enamines (subsection 1) indicates[56] that migration of such a bond from an exocyclic to an endocyclic position (on protonation at the β-carbon atom) is energetically most favourable for six-membered and unfavourable for five-membered rings. For enamines of type (XXIV) it is assumed[57] that, in contrast to (XIV), they are protonated not at the β-carbon atom but mainly at the nitrogen atom, owing to steric hindrance to conjugation. From the concept of *I*-strain it would be expected that the six-membered compound would be more basic. Actually, however, the opposite situation is observed[57]: pK_a is respectively 8.71 and 8.34 according as n has the value 1 or 2 in (XXIV)†. A possible reason is that in the former case steric hindrance to conjugation is smaller and the contribution of *C*-protonation to the effective ionisation constant larger: hence the enhanced basicity of the five-membered enamine. The above view is confirmed by study of the protonation of enamines of this type[58]. Five-membered are more basic than six-membered enamines of type (XXV) also[59], apparently owing to diminished angular stress accompanying *C*-protonation of the former. A marked change in basicity with ring size is observed[60] also for enamines of a fourth type:

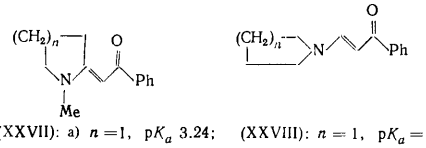


(XXVI)

$n=2$, $\Delta pK_a(MeNO_2) = 3.93$;
$n=3$, $\Delta pK_a(MeNO_2) = 1.6$

The lower the basicity of the six- than of the seven-membered enamine is due to a smaller contribution of *C*-protonation to the ionisation constant of the former compound.

Unusual results have been obtained[61] in a study of the basicity of the enamino-ketones (XXVII) and (XXVIII):



(XXVII): a) $n = 1$, pK_a 3.24; b) $n = 2$, pK_a 5.22; c) $n = 3$, pK_a 4.3

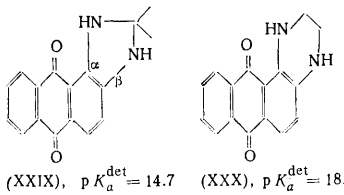
(XXVIII): $n = 1$, $pK_a = 2.08$; $n = 2$, $pK_a = 2.11$; $n = 3$, $pK_a = 1.83$

The dependence on ring size in the series (XXVII) is the same as for the enamines (XIV), but that in (XXVIII) is considerably smaller. These facts, as well as the sharp fall in basicity on passing from (XXVII) to (XXVIII), have been explained by studying the protonation of these compounds: the former undergo *C*-protonation, but the latter *N*- and *O*-protonation[61].

We have been considering research on heteromonocyclic compounds, but several studies have been made of the ionisation constants of fused heterocycles. An interesting investigation of the properties of tetracyclic derivatives containing an anthraquinone fragment has revealed[62] a considerable difference in acidity between the compounds

¶ The same sequence is maintained for other compounds (amidines, lactams[34,35]) which, like the enamines (XIV), are protonated at an exocyclic atom.

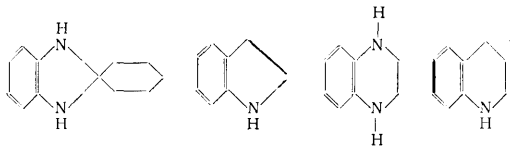
† These differences were not discussed[57].



(XXIX), $pK_a^{det} = 14.7$ (XXX), $pK_a^{det} = 18.9$

the former, containing a strained five-membered ring, is a stronger acid than its six-membered analogue (XXX) by a factor of ~10^4. This is explained[62] in terms of the enhanced *p*-character[17,18] of the orbitals of atoms α and β forming the strained ring: hence the N : H orbital of (XXIX) has an enhanced *s*-character, which is responsible for the increased acidity of this compound.

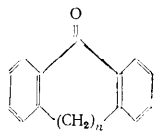
Among other examples of nitrogen heterocycles the five-membered compounds (XXXI) and (XXXII) are stronger acids than their six-membered analogues (XXXIII) and (XXXIV) [63]:



	(XXXI)	(XXXII)	(XXXIII)	(XXXIV)
pK_a^{det}	29.3	30.5	32.1	32.1

In explaining such effects we must also bear in mind that the better conditions of solvation of the anion of a five-membered ring may play an important part.

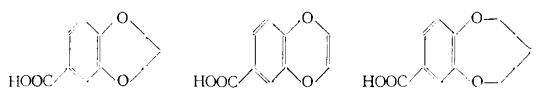
In contrast to basicity measurements on unsaturated[47] (above) and saturated ketones, in which the influence of ring size is insignificant, the fused cycloalkanones



(XXXV)

show a decrease in basicity with ring size[64] in the sequence $C_6 > C_7 \cong C_8 > C_5$.

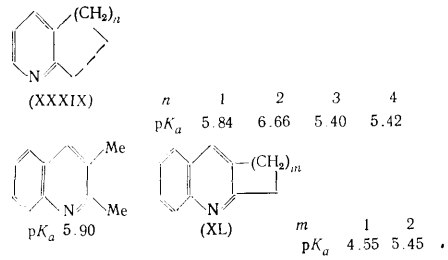
Measurements on a series of oxygen-containing bicyclic compounds showed[65] that the seven-membered is the strongest acid, and the five-membered the weakest:



	(XXXVI)	(XXXVII)	(XXXVIII)
pK_a	4.50	4.35	4.23

This was attributed to two effects—conjugation of the lone pair of the oxygen atom *para* to the carboxyl and the negative inductive effect of the second oxygen atom on the first—both of which are largest for the five-membered ring and smallest for the seven-membered ring. The former effect produces a decrease in acidity with ring size in the sequence $C_7 > C_8 > C_5$, and the latter effect in the sequence $C_5 > C_6 > C_7$. Superposition of these effects gave[65] the experimental situation $C_7 > C_6 > C_5$, with a relatively small influence of ring size on acidity (the need to consider both effects follows from results for hydrolysis of the ethers (XXXVI)–(XXXVIII), which will be discussed in section III, 3).

The greater electron-accepting influence of a small, strained ring on an adjacent position in a fused aromatic ring agrees well with basicity data for annelated pyridines (XXXIX) [66] and quinolines (XL) [67]:



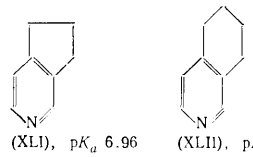
(XXXIX)

n	1	2	3	4
pK_a	5.84	6.66	5.40	5.42

pK_a 5.90 (XL)

m	1	2
pK_a	4.55	5.45

Comparison of similar data with ^{13}C n.m.r. spectra reveals[20] the interesting fact that, when the fused ring is attached at positions 3 and 4 instead of 2 and 3 of the pyridine ring, the five-membered are more basic than the six-membered compounds:



(XLI), pK_a 6.96 (XLII), pK_a 6.83 .

It is suggested[20] that atoms located β to the strained ring are enriched with electrons. In other words, the *p*-character of orbitals in this position is assumed to be enhanced (this is not mentioned in Ref. 20). Although these considerations seem to be consistent with the ^{13}C n.m.r. data, considerably more experimental results will be required to confirm them.

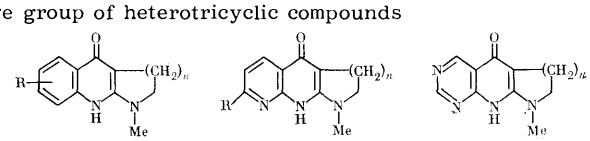
Measurement of the ionisation constants of series of hydrogenated furo- and pyrano-[2,3-*b*]pyridine derivatives has shown[68] that for the *N*-unsubstituted compounds (XLIII) and (XLIV) the five-membered system is much more strongly acid than the six-membered, but they are equally basic:



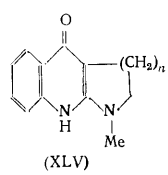
(XLIII), pK_a^{det} 8.92; pK_a^{add} 1.95 (XLIV), pK_a^{det} 10.17; pK_a^{add} 1.94 ,

The former effect is apparently due to the influence of the strained five-membered ring on the adjacent position (NH) of the aromatic ring, and the latter to protonation at the exocyclic oxygen atom. The same explanation applies to the closely similar basicities of the *N*-methyl derivatives contrasted with the less basic five-membered than six-membered methoxy-derivative (pK_a respectively 1.84 and 3.04).

Finally, a recent study of the ionisation constants of a large group of heterotricyclic compounds



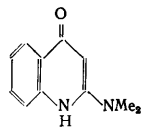
has shown fairly weak basic and acidic properties with protonation occurring at the oxygen atom[69,70]. An example is provided by the data obtained[69] for the quinoline derivatives



(XLV)

n	1	2	3
pK_a^{add}	5.60	5.31	4.97
pK_a^{det}	12.55	12.65	12.70

which fit well into the above schemes: the basicity is maximal, since electrons of the nitrogen atom in the five-membered ring are conjugated best, while the maximum acidity of the compound containing a five-membered ring is explained by Streitwieser rehybridisation of the orbitals, as has already been discussed several times. However, comparison of these data with pK_a measurements for 2-dimethylaminoquinol-4-one



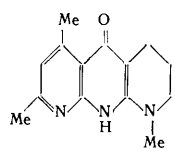
(XLVI)

pK_a^{add} 5.60;
pK_a^{det} 11.92,

reveals that the results cannot be explained in terms of the Finnegan-Streitwieser concept (the pattern is preserved for compounds containing a substituent such as chloro or nitro at position 6 in the benzene ring). Indeed, on this view compounds containing a fused five-membered ring should be far stronger acids than bicyclic compounds of type (XLVI). With regard to basicity, too, the ultraviolet spectra would suggest that the six-membered compound (XLVI) would be more basic, whereas for compounds of type (XLV) (and their chloro-derivatives) and (XLVI) the opposite pattern is in fact observed.

In order to interpret these results it was suggested[69,70] that an important (if not leading) role is played by the ability of the solvent to solvate cations and anions on protonation and deprotonation respectively. On this hypothesis acid and basic strengths in this series of compounds are determined by steric hindrance to solvation, such hindrance being least for five-membered rings on protonation, but on deprotonation for compounds devoid of a third, fused ring (XLVI).

To confirm these views, basicity and acidity measurements were made[70] on the 1,8-naphthyridine derivative

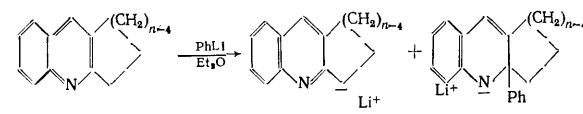


(XLVII)

pK_a^{det} 12.86; pK_a^{add} 4.61

containing methyl groups at positions 2 and 4 of the pyridine ring. As was to be expected, this compound proved to be less basic than the benzene analogue (XLV: $n = 2$) (pK_a 5.31), owing to the stronger electron-accepting influence of the annelated dimethylpyridine than of the benzene ring. Introduction of methyl groups at α and γ positions of the pyridine ring does not affect solvation of the protonated form, where the chief role belongs to solvation of the positive charge concentrated mainly on the nitrogen atom of the middle pyridone ring. On the other hand, solvation of the negative charge on the pyridone oxygen atom is the main factor for the anion, and the vicinity of a bulky methyl group should have an appreciable effect. These conclusions and hypotheses agree well with experimental results: the acidity of (XLVII) is even lower (despite the electron-accepting effect of the pyridine ring) than that of the benzene analogue (XLV: $n = 2$) (pK_a 12.65).

In concluding this subsection we consider the reaction of fused quinolines (XLVIII) with phenyl-lithium, which indicates the acidity of the corresponding α-methylene groups[71]:



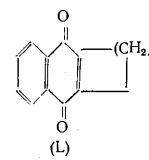
(XLVIII) (XLIX)

n	Yield, %	
1	97	< 1
2	96	< 1
3	61	31
4	33	48

It is assumed[70] that the acidity of the methylene groups is much lower for seven- and eight-membered rings, owing to steric inhibition of resonance in the resulting anion. A competitive process involving formation of the compounds (XLIX) is therefore observed with these rings.

3. Polargraphy

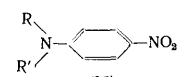
The polarographic reduction of C_5–C_{16} bromocycloalkanes gives a curve[74] similar to that obtained earlier for S_N2 solvolytic reactions. The five-membered compound is reduced most readily, and the six-membered compound with greatest difficulty (bromocycloheptanone occupies an intermediate position)[74], in good agreement with the concept of *I*-strain. For the fused cyclic compounds



(L)

n	1	2	3
$-E_{1/2}$, V	0.695	0.748	0.854

the variation in ease of polarographic reduction agrees well[75] with the Finnegan–Streitwieser concept. In the case of nitrobenzenes containing *p*-diethylamino, *p*-pyrrolidino, or *p*-piperidino



(LI)

a) R = R′ = Et, $E_{1/2}$ = −0.625 V;
b) RR′ = $(CH_2)_4$, $E_{1/2}$ = −0.619 V;
c) RR′ = $(CH_2)_5$, $E_{1/2}$ = −0.599 V.

on the other hand, the six-membered compound is reduced more readily, since the pyrrolidine ring conjugates better with the benzene ring, i.e. is a stronger electron donor[50].

The polarographic behaviour of enamines (XIV: $n = 1$–3) shows[76] small but definite differences in half-wave potentials depending on ring size, with six-membered most readily reduced, and five-membered enamines with the greatest difficulty. This is explained[76] in terms of *I*-strain on the hypothesis that reduction to the radical-anion involves enhancement of the *p*-character of the radical centre. It was shown in the same and a subsequent paper[77] that this is apparently a general rule and can be used to indicate the site of reduction of an enamine (i.e. whether a ring atom or a side-chain is attacked by the electron) and the structure of the radical-anion.

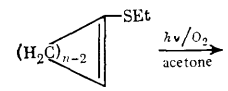
III. RING SIZE AND REACTIVITY

1. Oxidation and Reduction

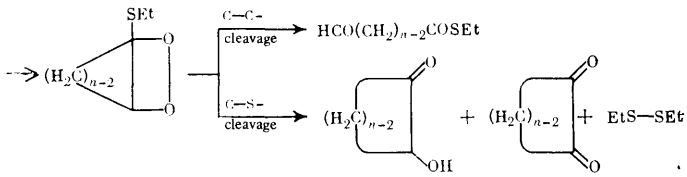
Rates of oxidation of cycloalkanes[78] and their derivatives by various reagents decrease with ring size in the sequence $C_8 > C_7 > C_5 > C_6$, which on the whole is consistent with the concept of *I*-strain[79]. However, the differences in rates of oxidation are far smaller than those in rates of solvolysis,

from which it was concluded that oxidation involves not formation of a carbonium ion but homolytic fission of a carbon-carbon bond[78].

Among cycloalkenes cyclohexene undergoes more rapid autoxidation than does cycloheptene, while cyclopentene is the most difficult to oxidise[80]. In contrast, rates of ozonolysis of cycloalkenes diminish in the sequence cyclopentene > cycloheptene > cyclohexene[81]: i.e. on the assumption that the reaction involves an $sp^2 \rightarrow sp^3$ change in configuration of the cyclic carbon atoms, this sequence is the opposite to that to be expected on the basis of *I*-strain. The direction of the photo-oxidation of cyclic vinyl sulphides (LII) depends considerably on ring size[82]:

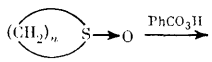


(LII)

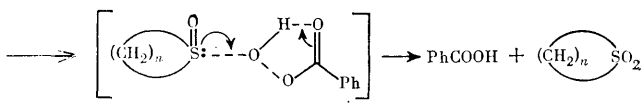


Carbon–carbon cleavage takes place almost quantitatively in unstrained six-membered and little strained twelve-membered rings[82].

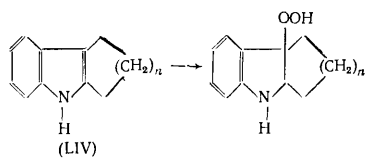
The rate of oxidation of cyclic tertiary amines, with slow intermediate formation of a planar radical-cation, decreases[83] in the sequence *N*-methylhexamethyleneimine > *N*-methylpyrrolidine > *N*-methylpiperidine. The oxidation of cyclic sulphoxides in acid and alkaline media



(LIII), $n = 3$–5



diminishes with ring size[84] in the sequences $C_6 > C_4 > C_5$ (pH 3.2–3.6) and $C_6 \cong C_4 > C_5$ (pH 11.85), the differences in rate being small. Finally, the dependence of rate of oxidation of polymethyleneindoles



(LIV)

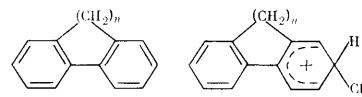
on ring size agrees well with the concept of *I*-strain[85].

Several studies have been made of the dependence of rate of reduction on ring size. Reduction of cycloalkenes by various methods gives a sequence of variation in rate (cycloheptene > cyclopentene > cyclohexene) the direct reverse of what might be expected on the basis of *I*-strain. It was supposed[86] that the main factor here is not change in hybridisation of the cyclic atoms but change in torsional and angular strains and the effect of α-substitutents. The dependence of rate of hydrogenation of cycloalkanones on ring size ($C_6 > C_5 > C_7$) suggests[87] change in hybridisation $sp^2 \rightarrow sp^3$ of the carbonyl carbon atom at slow stage. Other workers[88,89] have obtained similar results for the hydrogenation of cycloalkanones.

Among the compounds (LIa–c) the six-membered derivative is reduced far more rapidly[50], because of the difference in conjugation of pyrrolidine and piperidine rings with the benzene ring (Section II,3). The reduction of cyclic sulphoxides[90], which probably has an S_N2 mechanism, gives the expected dependence $C_5 > C_7 > C_6$ of rate on ring size. The negative entropy of activation increases as the ring becomes larger[90], because small and five-membered rings are quite rigid in the ground state, and the degree of order in the activated complex does not increase so substantially as in six- and seven-membered rings.

2. Reactions with Electrophilic Reagents

Bromination[91], nitration[91,92], and isotope exchange[93] in indane and tetralin show that, when a strained fused ring is present, electrophilic substitution occurs to a considerably greater extent at a β- than at an α-position, in good agreement with the above Finnegan–Streitwieser concept. This effect does not operate[94] in the chlorination of tricyclic compounds (LV)



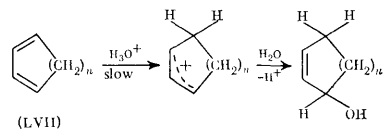
(LV) (LVI)

where the ability of the second benzene ring to stabilise a transition state of type (LVI) is the most important factor. Values for (LV) of the angle θ of the twisting of the second benzene ring from the plane of the first and the relative rates of chlorination

n	1	2	3	4
θ	0	16	49	67
k_{rel}	300	26.6	1.3	0.84

demonstrate[94] the importance of coplanarity of the two aromatic rings in reactions of this type.

Protodesilylation of benzocyclobutane, indane, and tetralin derivatives also gives the expected results[95]: the presence of a strained fused ring directs electrophilic addition of a proton (the rate-determining stage) mainly at a β-position (Section I). The main factor in the addition of various reagents at the double bond in cycloalkenes is apparently (as in reduction) not the change in hybridisation but the overall change in strain in the rings: in such cases addition to cyclopentene is more rapid than that to cyclohexene[96]. On the other hand, the highest rate of hydration of dienes in acid medium is observed with the six-membered compound[97]:



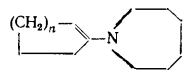
(LVII)

n	1	2	3	4
k_{rel}	200	2000	4	1

These workers remark[97] that a model of *I*-strain fits nucleophilic substitution better than electrophilic substitution: differences in the dependence on ring size are substantially smaller in the latter case. This is attributed[97] to a smaller

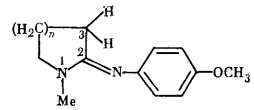
degree of rehybridisation in the transition state involved in electrophilic substitution.

Several studies[98-100] of the alkylation of cyclic enamines have shown in all cases that attack at a cyclic carbon atom (*C*-alkylation) occurs more readily with five-membered compounds, owing to the stronger conjugation of the lone pair of the pyrrolidine nitrogen atom with the enamine double bond. The rate of deuterium exchange K^D_{rel} of a vinyl proton in enamines also depends on ring size[101]:



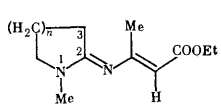
n	1	3
k^D_{rel}	5.95	1.98

Dependence of rate of deuterium exchange of protons in perdeuteromethanol at position 3 on the size of a saturated nitrogen heterocycle has been observed also in series of amidines and enamidines[102,103]:



(LVIII)

n	1	2	3
10^5k, s^{-1}	13.02	51.69	6.48

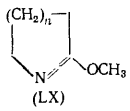


(LIX)

n	1	2	3
10^5k, s^{-1}	1.44	3.77	0,25

On the assumption that the reaction involves tautomeric enamines with the double bond at position 2 or 3, rehybridisation of carbon atom 3 takes place in the rate-determining stage, and the resulting series corresponds to the variation in *I*-strain.

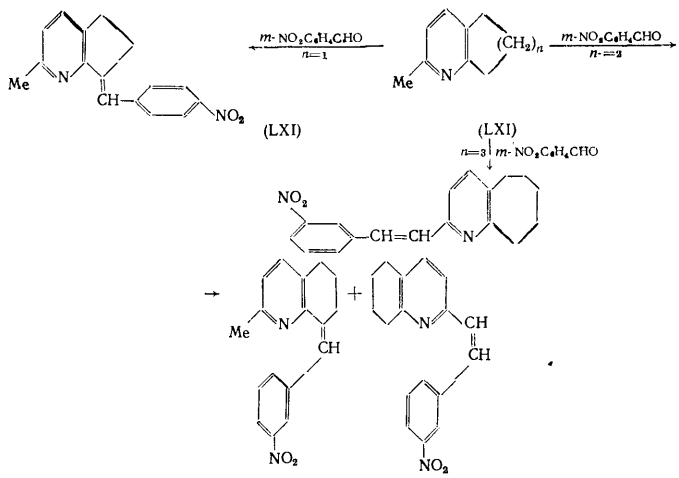
Small but definite differences have been observed[104] in the alkylation of lactim ethers with dimethyl sulphate:



(LX)

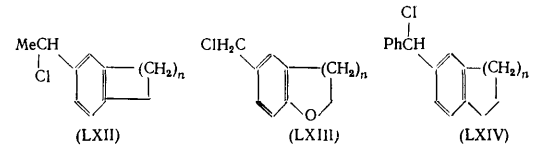
n	1	2	3
k_{rel}	1.36	1.13	1

Rehybridisation does not occur, and *F*-strain is apparently responsible for the variation in rate. The action of aldehydes on 2,3-polymethylenepyridines (LXI) depends[105,106] on the length of the polymethylene chain:



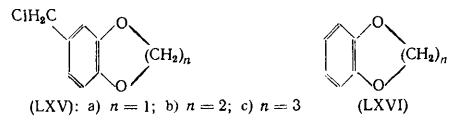
3. Reactions with Nucleophilic Reagents

Most of the work concerned with the problem covered in this Review has been devoted to reactions of cyclic compounds with nucleophilic reagents[107-131], and most of these investigations have studied various types of solvolytic reactions. Thus the rate of solvolysis of the chlorine atom in (LXII)



(LXII) (LXIII) (LXIV)

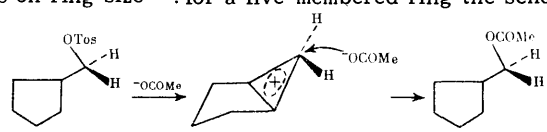
decreases in the sequence $C_5 > C_4 > C_6$.[92] The same rules for five- and six-membered rings had been observed earlier in oxygen-containing bicycles (LXIII)[25] and the compounds (LXIV)[107]; in the latter case the effect was explained in terms of hyperconjugation. For the bicyclic compounds (LXVa-c)



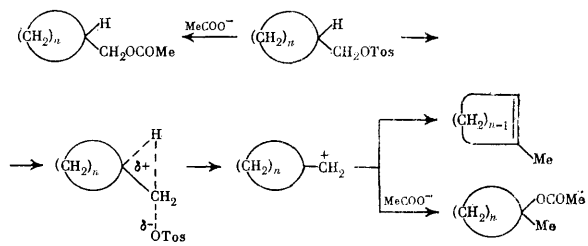
(LXV): a) $n = 1$; b) $n = 2$; c) $n = 3$ (LXVI)

the relative rates of solvolysis were 10 : 6 : 1.[108] What these workers[108] regarded as the two main effects in this system (conjugation of the lone pair of the oxygen atom with the cationic centre and the inductive effect of the second oxygen atom) have already been discussed in detail (Section II,2). These same effects determine the relative rates of hydrolysis of the complex ethers (LXVI).[65] The solvolysis of cycloalkyl bromides (as well as their reaction with the iodide anion) is fully consistent with the concept of *I*-strain[109].

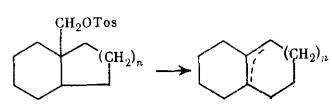
The solvolysis of cycloalkylmethyl toluene-*p*-sulphonates depends on ring size[110]: for a five-membered ring the scheme



has been suggested; and for larger rings



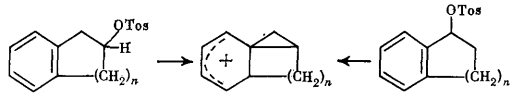
It is evident that in all cases a planar configuration of the cyclic carbon atom should arise at an intermediate stage, so that the rate of solvolysis varies with the *I*-strain: $C_5 > C_7 > C_6$. The solvolysis of toluene-*p*-sulphonates (or *p*-nitrobenzoates) in the different type of system (LXVII) is also appreciably more rapid in the five-membered compound[111]:



(LXVII)

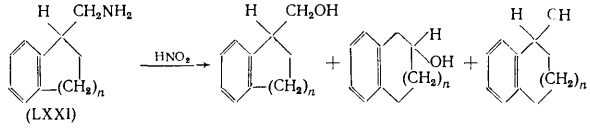
n	1	2
k_{rel}	1500	3.9

An interesting comparison has been made of the solvolysis of the toluene-p-sulphonates (LXVIII) and (LXIX), in which the same mechanism with intermediate formation of a phenonium ion (LXX) is involved[112]:



(LXVIII) (LXX) (LXIX)

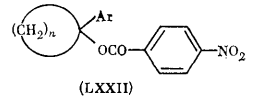
The rate constants (10^5k, s^{-1}) of formolysis of (LXVIII) are 27.3 (6), 152 (7), 2250 (8) (ring size in parentheses). Such successive increase in rates was attributed[112] to decrease in the angular strain in the cation (LXX). However, a different variation in rate applies to the process (LXIX) → (LXX): 2.51 (5), 6.80 (6), 1.80 (7), 0.18 (8). These results were interpreted[112] on the basis of molecular models: only axial isomers can be converted into (LXX), but because of conformational factors the existence of such isomers is unfavourable for seven- and especially eight-membered compounds. The same conformational effects determine the composition of the products in the deamination of amines (LXXI)[113]:



(LXXI)

n		Yield, %	
1	—	85	15
2	38	62	—
3	—	45	53
4	—	<5	54

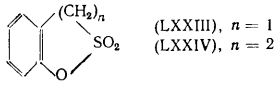
A closely related investigation of the hydrolysis of *p*-nitrobenzoates (LXXII)[114] has given results agreeing well with the concept of *I*-strain:



(LXXII)

n	3	4	5	6	7
k_{rel}	0.426	178	1	51.5	515

An attempt has been made[115] to relate rates of hydrolysis of lactones and cyclic toluene-*p*-sulphonates with the strain in the rings. However, a correlation has been observed only for the pair

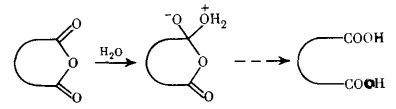


(LXXIII), $n = 1$
(LXXIV), $n = 2$

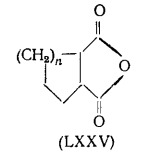
the five-membered ring is more stressed by ~100 kJ mole^{-1}, and is hydrolysed more rapidly by a factor of 10^4.

In aqueous ethanol five-membered anhydrides are hydrolysed rather more rapidly than the six-membered compounds, whereas in an alkaline medium glutaric anhydride is hydrolysed slightly more rapidly[116]. In contrast to this closeness of the rates of hydrolysis of anhydrides the differences for lactams and especially lactones and thiolactones are incomparably larger[116], and agreement with Brown's views (*I*-strain) is better. Various degrees of change in hybridisation in the transition state were assumed[116] to be possible, and these changes determined the relative rate constants of six- and five-membered compounds. The rate of the reverse reaction—cyclisation of acid esters into anhydrides—is much higher for the five-membered ring, apparently because of the entropy factor, consisting in better steric conditions for closure of such a ring[116].

Rates of hydrolysis of succinic and glutaric anhydrides at pH 5.2 and 20 °C are almost equal[117]. This is interpreted in terms of *I*-strain, with respect to which the situation in the transition state is more favourable of the six-membered ring:



On the other hand, succinic anhydride is characterised by an extremely strained ground state (three sp^2-carbon atoms), which facilitates addition of water. The superposition of these effects gives almost the same rate constants for the five- and six-membered rings. Results in the same paper[117] for the effect of the size of the fused ring on the rate of hydrolysis of anhydrides

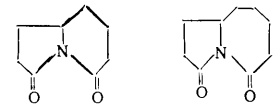


(LXXV)

n	1	2	3
k, min^{-1}	1.13	0.381	0.185

show that the effect is due to steric hindrance (by the methylene groups) to attach by water in seven- and six-membered in comparison with five-membered anhydrides.

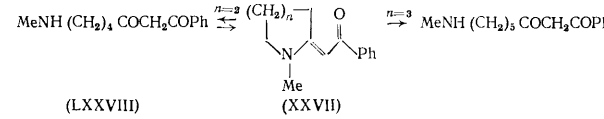
For *N*-methyl-succinimide, -glutarimide, and -adipimide rates of hydrolysis fall in the sequence $C_6 > C_7 > C_5$, with not very large differences ($k_6 : k_7 : k_5 = 2.6 : 1.5 : 1$).[118] Hydrolysis of the bicyclic imides



(LXXVI); 85.7% (LXXVII); 66.1%

in an alkaline medium occurs preferentially at the six- and seven-membered rings (degrees of hydrolysis given for 20 °C).[118]

Among enamines, compounds containing a six-membered ring are hydrolysed appreciably more rapidly in the pH range in which addition of water ($sp^2 \rightarrow sp^3$ transition for the β-carbon atom) limits the rate[119,120]. Rates of hydrolysis of the enamines (XXVI) depend significantly on ring size[60, 121], owing to the difference in the site of their protonation in strongly acid media. Detailed polarographic study[122] of the hydrolysis of the enamino-ketones (XXVII) has established that in 0.1*N* hydrochloric acid only the seven-membered (XXVIIc) is hydrolysed quantitatively, the equilibrium (XXVIIb) ⇋ (LXXVIII) being established for the six-membered compound:

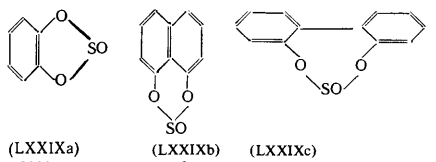


(LXXVIII) (XXVII)

the five-membered (XXVIIa) is not hydrolysed. Such differences are explained by acceleration of the reverse reaction on passing from the seven- to the six- and then the five-membered ring as a consequence of the entropy factor. The rate constant of the forward reaction (hydrolysis) for the six-membered ring (9×10^{-4} s^{-1}) is about double that for the seven-membered ring. Heating (XXVIIa and b) in an acetate buffer results in acid cleavage (with formation of benzoic acid), the rate of which is lower for the five- than for the six-membered ring (10^4k respectively 1.63 ± 0.37 and 6.2 ± 1.9 s^{-1}). Heating (XXVIIa–c) in 0.1*N* sodium hydroxide yields acetophenone, the rate decreasing in the sequence $C_6 > C_7 > C_5$.

The kinetics of the alkaline hydrolysis of amidines[53] is not consistent with the concept of *I*-strain: the rate of hydrolysis falls in the sequence $C_5 > C_6 \gg C_7 > C_8$. In the

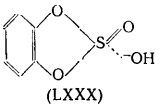
alkaline hydrolysis of cyclic sulphites the five-membered compound is hydrolysed most rapidly, and the seven-membered compound most slowly[123]:



(LXXIXa) (LXXIXb) (LXXIXc)

$10^6\ k,\ s^{-1}$	2000	16	2.9

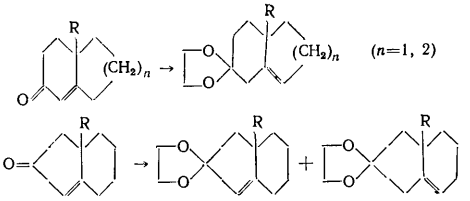
The explanation given[53] for these results is that attainment of a transition state of type



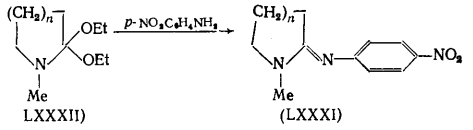
(LXXX)

is more favourbale for the planar five-membered ring. An alternative explanation can be based on repulsion of the hydroxide anion and the lone pair of the oxygen atom (as already discussed for lactones)[124], which diminishes in the sequence $C_7 > C_6 > C_5$.

Results[125,126] on the formation of hemiacetals and acetals of cyclic ketones agree well with concept of *I*-strain. An extremely interesting investigation[127] on migration of a double bond during acetalisation as a function of ring size has shown that, if the carbonyl group is present in a six-membered ring, 100% migration into the other ring takes place, whereas in a five-membered ring a mixture is formed:



It has been established[128] by a method of competing reactions that the rate of formation of amidines (LXXXI) by the action of primary amines on lactam acetals (LXXXII) depends on ring size, varying in the sequence $C_5 > C_7 > C_6$:

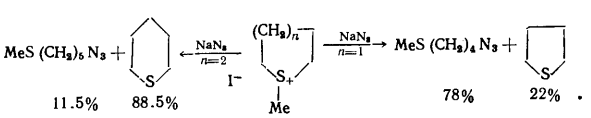


LXXXII) (LXXXI)

n	1	2	3
k_{rel}	28	1	8.3

The reaction mechanism was not studied specially, but the above relation corresponds to a change in hybridisation of the cyclic carbon from sp^3 to sp^2.

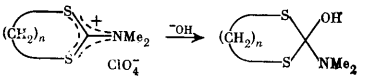
In the action of sodium azide on onium salts, e.g. (LXXXIII), the five-membered ring undergoes cleavage, wheras a six-membered ring is preserved:



(LXXXIII)

It was assumed[129] that the cleavage of an unstrained five-membered ring is more favourable than that of an unstrained six-membered ring, and that attack on the unshielded carbon atom 2 in the saturated ring is more favourable for the five-membered ring. Six-membered compounds are characterised by attack at the exocyclic methyl group.

Maximum and minimum rates of reaction of dithiolonium salts

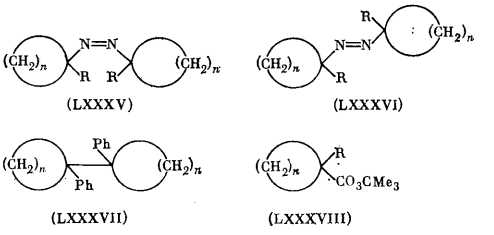


(LXXXIV), $n = 2-4$

are exhibited by seven- and five-membered compounds respectively, which is regarded[130], as corresponding to an increase in stability of the ground state in this sequence ($C_5 > C_6 > C_7$).

4. Radical Reactions

Capture of a hydrogen atom by various radicals (butoxy, bromine, chlorine, phenyl, etc.) on reaction with cycloalkanes gives a sequence of diminishing reaction velocity $C_5 \cong C_7 > C_6 > C_8 > C_9$ corresponding well to formation of a planar (sp^2) radical centre[132]. Similar results have been obtained for the detachment of a bromine radical from cycloalkyl bromides[133]. A series of studies[134,135] of the formation of radicals by the thermolysis or photolysis of *cis*- and *trans*-azo-compounds (LXXXV) and (LXXXVI), biscycloalkanes (LXXXVII), and peroxides (LXXXVIII)



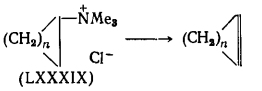
(LXXXV) (LXXXVI)

(LXXXVII) (LXXXVIII)

has established that, although the concept of *I*-strain applies well to (LXXXVI) and (LXXXVII), with (LXXXVIII) the dependence of rate on ring size is quite insignificant, but for (LXXXV) the rate increases monotonically. The explanation is that the variation in rate depends on the extent to which hybridisation of the reaction centre has changed in the transition state, i.e. whether the latter resembles the initial or the final state. It is necessary[135] to take into account *F*-strain as well as *I*-strain.

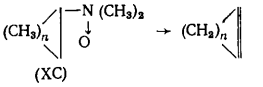
5. Elimination Reactions

Relatively few investigations have been made on the influence of ring size on rate of elimination. In that of trimethylamine from salts



(LXXXIX)

the rate varies in the sequences $C_5 > C_7 > C_6$ and $C_7 > C_5 > C_6$ in the presence of potassium t-butoxide and ethoxide respectively[136,137]. The suggested reaction mechanism involves formation of a planar activated complex, which is energetically unfavourable for six-membered and favourable for five- and seven-membered compounds. Similar results (with the same interpretation) have been obtained for the formation of cycloalkenes from *N*-oxides[138]

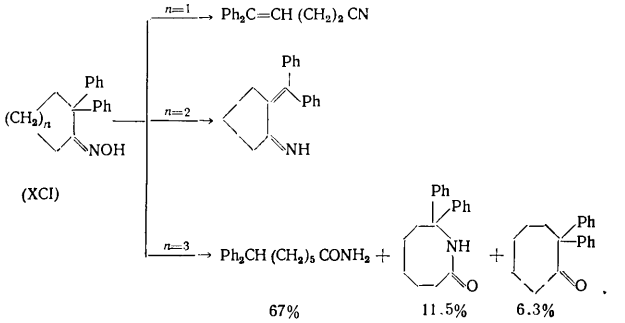


(XC)

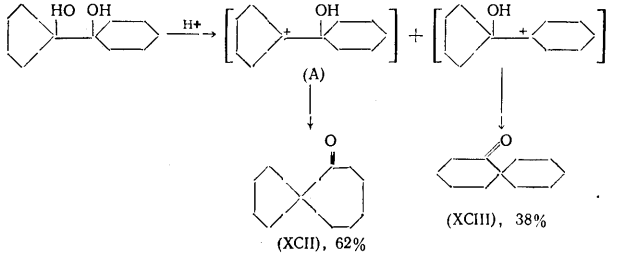
and also in the dehydration of cycloalkanols and the dehydrochlorination of cycloalkyl chlorides[139].

6. Rearrangements

It was shown in several studies[140-143] that the rate of the Beckmann rearrangement falls in the aqueous cyclohexanone > cycloheptanone > cyclo-octanone > cyclopentanone. If the rate determining stage is assumed to involve conversion of an exocyclic into an endocyclic carbon-nitrogen double bond, these results are consistent with Brown's generalisation that five-membered rings are especially likely to retain double bonds in an exocyclic position[42]. When oximes (XCI) are heated under the conditions of the rearrangement, considerable differences are observed[144] in the dependence on ring size, with preferential opening of strained five- and seven-membered rings:

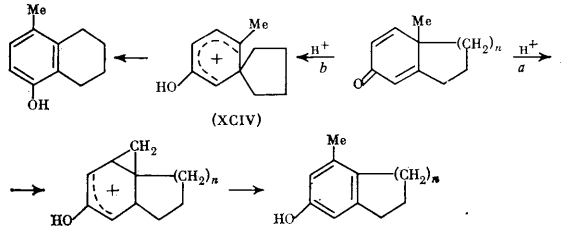


Important results have been obtained for the pinacoline rearrangement, clearly showing[145] that the first direction predominates when the carbonium centre is located in a five- or six-membered ring:



From our point of view formation of the cation (A) is still more favourable than would follow from the relative yields of reaction products (XCII) and (XCIII), since the entropy factor promotes closure of a six-membered (XCIII), not a seven-membered (XCII), ring. This factor must be taken into account in other cases as well (e.g. in the rearrangement of a compound containing five- and seven-membered rings), but the conclusion from the above work seems to be valid—that a carbocation centre is more readily localised on cyclic atoms of five- and seven-membered than of a six-membered ring.

The dienone–phenol rearrangement also depends on ring size:

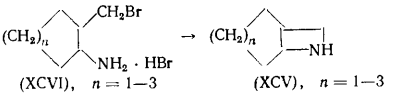


Only reaction path (*a*) is followed by the five-membered ring, since a four-membered spiro-compound of type (XCIV) is apparently unstable[146].

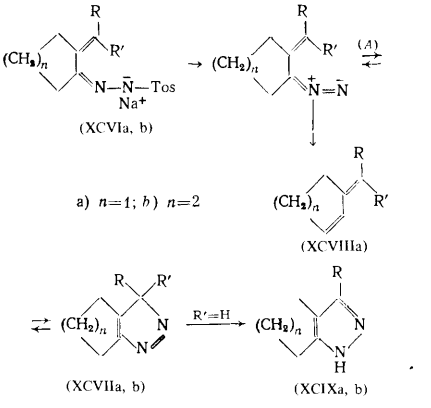
The rate of rearrangement of toluene-*p*-sulphonates of 1-hydroxymethyl-1-phenylcycloalkanes (into benzylcycloalkenes and benzylidenecycloalkanes) accompanying acetolysis decreases in the sequence $C_6 > C_5 > C_3 > C_4$.[147] The rate of isomerisation of methylenecycloalkanes into cycloalkenes[148,149] diminishes with ring size in the sequence $C_4 > C_5 >$ acylic cpd. $> C_6$. The slow stage is apparently formation of an anion with rehybridisation of the corresponding orbital.

7. Heterocyclisation

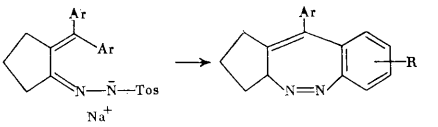
Formation of fused azetidines



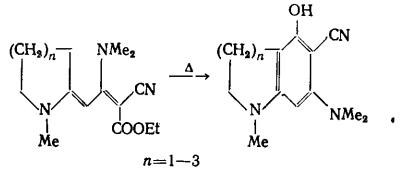
is most rapid for the seven-membered and slowest for the six-membered compound[150]. The increased rate of closure of (XCVI: $n = 3$) is attributed to greater conformational mobility of the seven-membered ring. Distinct differences are observed[151] in the cyclisation of toluene-*p*-sulphonylhydrazones (XCVIa, b):



If R, R′ ≠ H, cyclisation of (XCVIa) yields only dienes, but that of (XCVIb) gives pyrazoles, since (XCVIIIa) is then unstable, equilibrium (*A*) is displaced to the left, and stabilisation is achieved with formation of the dienes (XCVIIIa). When R′ = H, stable pyrazoles (XCIXa, b) are formed. With R = R′ = Ar the direction of reaction is unchanged for six-membered compounds, but fused diazepines are formed from five-membered rings:

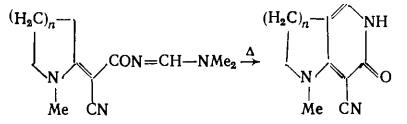


It has been established polarographically that in the formation of fused phenols from dienediamines six-membered compounds are cyclised most rapidly, and five-membered least rapidly[152]:

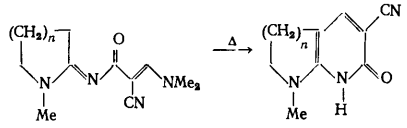


n=1–3

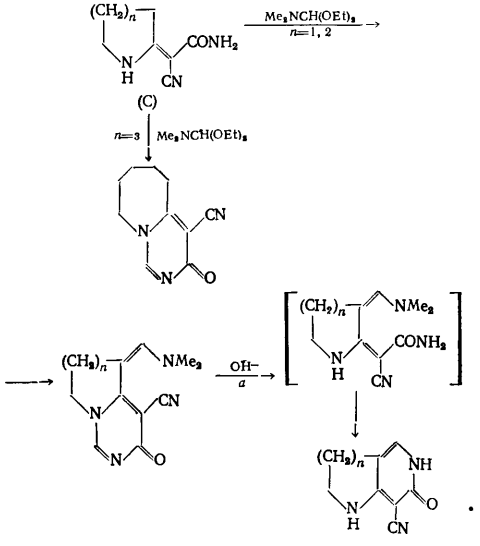
It has been shown by the same method that the rate of formation of fused pyrid-2-ones diminishes in the sequence $C_6 > C_7 > C_5$ [77]:



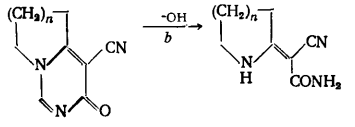
n	1	2	3
k_{rel}	1	249	28.6



Such variation in rate is due to rehybridisation of cyclic carbon from sp^2 to sp^3 on formation of the transition state (it is supposed that tautomers having a $C_{(2)}:C_{(3)}$ endocyclic double bond undergo cyclisation). In the reaction between enaminoamides (C) and dimethylformamide acetal different compounds are formed depending on ring size[153–155]:



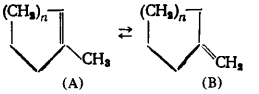
The ready cleavage of the pyrimidine ring observed in alkaline medium, with or without subsequent recyclisation (path *a* or *b*)



also depends on ring size, the rate varying in the sequence $C_5 \cong C_6 > C_7$.

IV. RING SIZE AND EQUILIBRIA

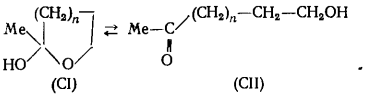
Investigation of the equilibrium between methylenecycloalkanes and methylcycloalkenes indicated that, in contrast to Brown's conclusion[5], the *endo/exo* ratio was higher for five- than for six-membered rings. The earlier assumption[158] was adopted[156,157] that the "greater substitution" of the double bond in tautomer (A) than in (B) is important:



(A) (B)

It is significant that the position of equilibrium is very largely determined by solvation, and in the gas phase the above ratio is close to unity.

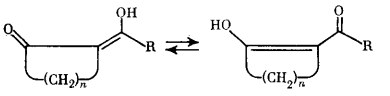
The leading role in the ring–chain equilibrium aminoketone ⇋ aminomethanol belongs to the entropy factor, and the cyclic form is observed only on formation of a five-membered ring[159]. When on cyclisation a larger number eclipsed interactions arise (in five-membered compounds), the situation levels off even for the equilibrium[160]



(CI) (CII)

Extremely contradictory results have been obtained for keto–enol tautomerism. Thus comparison of 2-benzoylindan-1-one with tetrahydronaphthalen-1-one reveals a much higher enol content in the five-membered compound[161], whereas in cycloalkanones and in acyl-lactones, -thiolactones, and -lactams[162–164] the quantity of the enolic tautomer diminishes on passing from the six- to the five-membered compounds. In 2-benzoylcycloalkanones[165], in contrast, the enol content decreases in the sequence $C_5 > C_7 > C_6$; in the enolic form the benzene ring is completely conjugated with carbonyl only in the five-membered compound.

Examination of the influence of ring size on the equilibrium



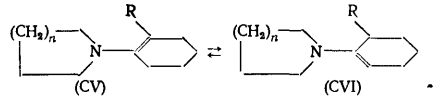
(CIII) (CIV)

shows[166,167] that tautomers having an endocylic double bond predominate in the six-membered compounds, followed by derivatives of cycloheptanone and cyclopentanone#.

The sequence $C_6 > C_8 > C_5 > C_7 > C_4$ in the rate of acid enolisation was explained[162] by the energetic advantage of formation of an endocylic double bond. However, the rate of basic enolisation of cycloalkanones varies in the different sequence $C_4 > C_5 > C_6 > C_7$, and it was correctly stated[162] that neither the advantage or disadvantage of formation of such a bond nor the concept of *I*-strain would explain such a sequence of decrease in rate of basic enoslisation. The explanation advanced[162] was that on passing from a seven- to a four-membered ring the s-character of the C–H orbital increases and ionisation of the C–H bond is facilitated, the latter being the rate-determining process in enolisation.

Similar relations have been observed[168] for the tautomerism of 2-acylcycloalkanethiones and 2-thioacylcycloalkanones.

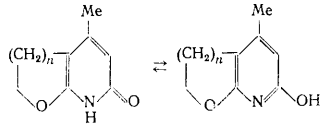
On the whole the view that exocyclic double bonds predominate with five-membered rings, and endocylic double bonds with six-membered rings[5], has now become fundamental in the interpretation of results for enamine–enamine tautomerism of the type[169,170]



(CV) (CVI)

With a substituent R capable of conjugation (COOAlK, $COCH_3$, COC_6H_5, etc.) the tautometer (CV) predominates with the five-membered ring, whereas the ratio of tautomers for the six-membered ring is close to unity. This was attributed[169,170] to a greater degree of conjugation of the former ring (associated with greater favourability of the resonance structure having an exocyclic N:C bond) and less steric hindrance to such conjugation (involving steric interaction of methylene protons of the pyrrolidine or piperidine ring with R). However, as has already been pointed out repeatedly[9], Brown's "exo–endo" generalisation[5] is not rigorous and is by no means always observed. For hydrazone–enehydrazine tautomerism in *NN*-dimethylhydrazones of ethyl 2-oxocycloalkanecarboxylates[171] the quantity of the latter tautomer (having an endocyclic double bond) increases in the sequence $C_7 < C_6 < C_5$, perhaps because conditions for intramolecular hydrogen bonding are best in a cyclopentenylhydrazine derivative.

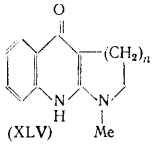
Lactim–lactam tautomerism



(XLIII), $n = 1$ (CVII)
(XLIV), $n = 2$

is another type exhibiting a distinct dependence of the position of equilibrium on ring size. Replacement of a dihydrofuran by a tetrahydropyran ring, both fused to a pyridone, leads to an appreciable decrease in the content of the lactim tautomer: the ratio of lactim to lactam decreases by factors of 15–20.[68] This was explained[68] by the Mills-Nixon-Brown effect (in the pyridone tautomer the double bond is localised in greater measure between the rings, which creates a more unfavourable situation for the five-membered ring: i.e. an endocyclic double bond is present) and by the electron-accepting influence of the strained ring, which increases the acidity of the nitrogen–hydrogen bond in (XLIII). Some uncertainty arises concerning the electron-accepting influence of five-membered compounds in the case of fused oxa- and aza-rings, since the degree of conjugation of the lone pair, in such case with the pyridone ring (electron-donor effect), is apparently highest also for these rings.

In another approach to the dependence of the position of lactim–lactam equilibrium the decrease in the content of lactim tautomers of the tricycles



(XLV)

n	1	2	3
Lactim, %	89	49	31

in the sequence $C_5 > C_6 > C_7$ has been attributed[172] to an accompanying diminution in the solvation of this tautomer, since hypothetical rehybridisation does not explain the differences between the six- and seven-membered rings. We can also try on this view to explain results for the equilibrium (XLIII), (XLIV) ⇆ (CVII). The orbital of the second pair of electrons of the oxygen atom (that of the first pair is perpendicular to the plane of the pyridine ring) is parallel to the nitrogen–hydrogen bond, and unfavourable shielding occurs with increase in the bulk of the substituent attached to the nitrogen atom (i.e. on solvation). For a six-membered ring, for which conjugation is less, the degree of shielding is also smaller, the lactam tautomer is better solvated, and the lactim content is appreciably diminished.

Finally, yet another equilibrium also characterised by dependence on ring size is the intermolecular association of lactams in non-polar solvents[173]: depending on the solvent the degree of association of lactams varies in the sequence $C_7 > C_5 > C_6$ (in tetrachloromethane, cyclohexane) or $C_5 > C_7 > C_6$ (benzene).

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From the above survey several considerations arise of which, in the Reviewer's opinion, insufficient account is taken in interpreting experimental results, especially when the concept of *I*-strain is used. Thus in processes involving $sp^2 \rightarrow sp^3$ rehybridisation very much depends on the size of α-substitutents in the ring and that of the attacking species. Steric hindrance to attack at a ring atom increases in the sequence $C_5 < C_6 < C_7$, which differs from the rate sequence $C_5 < C_7 < C_6$ to be expected from a model based on *I*-strain: i.e. inversion of rates for five- and seven-, six- and seven-, and even five- and six-membered compounds is by no means excluded. In reactions of the reverse type (change in hybridisation $sp^3 \rightarrow sp^2$), in which the sequence $C_5 > C_7 > C_6$ is to be expected, the presence of bulky substituents at the reaction centre may lead to unexpected acceleration of reactions with six- and especially seven-membered compounds.

It must also be stressed that the tendency of a reaction centre to be solvated has likewise only occasionally been discussed as a function of ring size, although in several cases solvation may exert an appreciable (and perhaps decisive) influence on the relative rates of processes. It is clearly an extremely complicated task to separate these effects.

In conclusion it must be noted that, despite the complexity of the questions and the hitherto inadequate predictive power of existing theoretical approaches, efforts aimed at solving the problem of the relation between ring size and the properties and reactivity of compounds have proved extremely fruitful and have enriched significantly both theoretical and synthetic organic chemistry.

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Phosphorylated and Thiophosphorylated Aminoheterocycles

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The review is devoted to the methods of synthesis, chemical reactions, reactivities, and transformations of phosphoryl- and thiophosphoryl-aminoheterocycles in living organisms and in the surrounding medium. Many of these substances are biologically active and are used in the national economy.
The bibliography includes 170 references.

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I. INTRODUCTION

Many derivatives of aminoheterocycles are used in various branches of the national ecomony; particular mention should be made of the use of sulphamidoheterocycles as medicinal drugs.. Phosphorylated and thiophosphorylated aminoheterocycles of similar structure also exhibit a varied biological activity. The nature of the activity is influenced significantly both by the nature of the heterocycle and by the structure of the phosphorus-containing residue. Phosphorylated and thiophosphorylated aminothiadiazoles[1], aminotriazoles[2-8], and aminothiazoles[1] have been patented as fungicides. Diethyleneaminophosphoryl-derivatives of 2- and 4-aminopyrimidines[9-12], aminopurine[13-15], 3-aminopyridazine[16], and 2-amino-1,3,4-thiadiazole[17-19] exhibit a carcinolytic activity against various strains of leukaemia and sarcoma. Data exist on the herbicidal and growth regulating activity of phosphorylaminothiazoles[20], phosphorylaminotriazoles[21], and phosphorylaminotriazines[22-27]; derivatives of 4-phosphazopyridazine also possess a herbicidal activity[28]. The weaker bactericidal activity of derivatives of phosphorylaminopyridine has been noted[29].

However, most phosphorylaminoheterocycles exhibit insecticidal and acaricidal activities. Derivatives of aminopyran[30], aminothietan[31-34], aminodithiolan[35-37], aminooxazole and amino-oxazoline[38-41], aminothiazole and aminothiazoline[38,41-48], amino-oxazine[41], aminotriazole[2,4,5,8,21], amino-1,3,4-thiadiazole and amino-1,2,4-thiadiazole[49,50], aminotriazine[51], and aminophenothiazine[52] have been described as insecticides and acaricides.

Some of the phosphoryl- and thiophosphoryl-aminoheterocycles have found practical applications as chemical plant protecting agents and medicinal drugs. 2-Diethoxythiophosphorylamino-1,3-dithiolan and 2-diethoxythiophosphorylamino-4-methyl-1,3-dithiolan under the commercial names "Cyolan" (dithiolene) and "Dithiolan" [53] are used as broad-spectrum insecticides against a group of pests on the cotton plant. 5-Amino-3-phenyl-1H-1,2-triazol-1-yl, *N*,*N*-dimethylphosphoramidate (triamiphos, vepsin) has been employed on a small scale as a systemic fungicide against powder mildew[53-57]. 4-Bromo-2-phenyl-5-(trimethoxyphosphazo)pyridazin-2-one (SGA 18796 preparation) has been tested as an experimental herbicide against weeds in sugar beet plantations[53]. Diaziridinyl 2-pyrimidinyl phosphoramidate (phosphamide) has been used in medical practice for the treatment of hypodermiasis[11]. The antitumour preparation 6-diaziridinylphosphorylamino-2-dimethylamino-7-methylpurine (fopurine) is effective against various forms of leukaemia in laboratory animals[58,59].

Bearing in mind the increasing importance of phosphorylated and thiophosphorylated aminoheterocycles for practical applications in the national economy, we thought it timely to compile this review of the literature data concerning the methods of synthesis and the chemical and physical properties of compounds of this class. The review covers the literature up to the middle of 1980.

II. METHODS OF SYNTHESIS OF PHOSPHORYLATED AMINOHETEROCYCLES

The commonest method of synthesising phosphoryl- and thiophosphoryl-aminoheterocycles is the reaction involving the phosphorylation of aminoheterocycles. Phosphoryl chloride, the chlorides and isothiocyanides of phosphorus acids, diphosphadithietans, acid phosphites, phosphorus pentachloride, etc. can be used as phosphorylating agents.

1. Phosphorylation with Chlorides of Tetracoordinate Phosphorus Acids

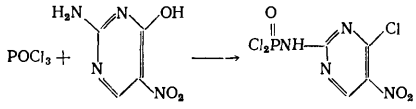
When phosphoryl chloride interacts with aminoheterocycles, the corresponding dichlorides of phosphoramidic acids are formed (Het is the residue of the heterocycle):

$$POCl_3 + H_2N\text{—}Het \xrightarrow[-HCl]{} Cl_2\overset{\overset{O}{\|}}{P}NH\text{—}Het \quad .$$

2-, 3-, and 4-Aminopyridines[10,60], 2- and 4-aminopyrimidines[10,12,61-65], 2-aminothiadiazoles[17,19,60,66], 2-aminobenzothiazole[67], 3-aminoindole[68], aminopurines[14,69], 3-aminopyridazine[70], creatinine[71], and sydnone imine[72] have been used as the initial aminoheterocycles. These reactions are usually carried out with refluxing in an excess of phosphoryl chloride for several hours and sometimes with heating in an organic solvent, for example, in benzene[64] or dichloromethane[72,73].

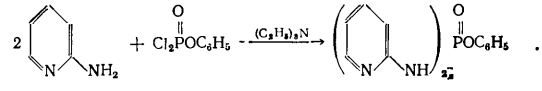
The reactions with secondary heterocyclic amines such as 2-alkylamino-1,3,4-thiadiazoles[18,19], 2-alkylamino-*sym*-triazines[24,73], and 2- and 4-alkylaminopyridines[74-76] proceed analogously. We may note that, when 6-chloro-2,4-bis-ethylamino-*sym*-triazine is refluxed with phosphoryl chloride for several hours, the products of the phosphorylation of only one amino-group are formed[23,25].

In the reaction with 2-amino-4-hydroxy-5-nitropyrimidine, phosphoryl chloride behaves not only as a phosphorylating agent but also as a chlorinating agent[77,78]:

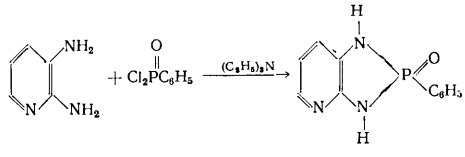


This method has been used to synthesise labelled compounds[15].

When phosphorus acids dichlorides were allowed to react with aminoheterocycles in the presence of tertiary amines, the corresponding phosphorus acid diamides were isolated[29,79,80]. *N*,*N*-di-(2-pyridyl)- and *N*,*N*-di-(2-pyrimidinyl)-*p*-nitrophenylphosphonodiamidates have been obtained in yields of 43 and 7% respectively by refluxing in dioxan 1 mole of *p*-nitrophenylphosphonic acid dichloride with 4 moles of the aminoheterocycle. Aryl *N*,*N*-di-(2-pyridyl)phosphorodiamidates have been obtained under similar conditions[29]:

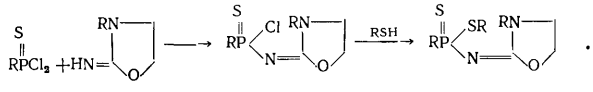


It is of interest to note that 2,4-diaminopyridine and the dichloride of phenylphosphonic acid react on heating in bromobenzene at 90–100 °C in the presence of an excess of a tertiary amine[81] to form a bicyclic condensation product:



4,5-Diaminopyrimidine does not enter into a similar reaction[81].

In many instances it is possible to achieve a controlled substitution of only one chlorine atom in the dichlorides of phosphonothionic acids by an aminoheterocycle residue and in such reactions the acid monochlorides are as a rule treated with nucleophiles without isolation in a pure form and the corresponding amidoesters of phosphonothionic acids are obtained. For example, the dithiophosphoryl derivatives of imino-oxazolidine are obtained by the reaction of the dichlorides of phosphonothionic acids with imino-oxazolidine and subsequent treatment with a thiol in the presence of sodium hydroxide[38,82]:



The reaction of the dichloride of chlorobutylphosphonic acid with 2-aminopyridine and subsequent hydrolysis with water in the presence of triethylamine yielded the acid ester of the corresponding pyridylphosphonamidic acid[83].

The reactions with the monochloride, ester, amide, and ester-amide derivatives of phosphorus acids with 2-, 3-, and 4-aminopyridines[29,84–88], 2- and 4-aminopyrimidines[85,89,90], 2-aminodithiolan and its salt[36], 2-iminodithiole and its salt[91], derivatives of 4-aminopyrazole[92], 2-aminoimidazoline[79], 2-aminothiazole[79,85,93,94], 3-alkyl-2-iminothiazolines[43,44,95], 2-aminothiazoline[79], 3-alkyl-2-iminothiazolidines[38,41,82,96–97], 2-imino-oxazolidines[38,41,82,96–98], 2-imino-1,3,4-thiadiazole[49], 3-alkyl-2-iminoperhydro-oxazines[38,41,97], 2-aminoquinoline[86], 2-aminobenzimidazole[99], 2-imino-1,3-dimethylbenzimidazoline[99], 2-aminobenzothiazole[85,99], 3-alkyl-2-iminobenzothiazoline[85,99], 2-aminobenzoxazole[99], 3-alkyl-2-iminobenzoxazoline[99], and 2-aminophenothiazine[52] have been investigated.

The reaction is carried out by heating a mixture of the phosphorus acid chloride with the aminoheterocycle or its salt in an organic solvent in the presence of a tertiary base and a double excess of the aminoheterocycle or an inorganic base, and also in a water–organic solvent two-phase system in the presence of alkali. The reaction and the yield of final products are influenced significantly by the structure of the phosphorus acid chloride, the basicity of the initial aminoheterocycle, and the nature of the solvent.

As a rule, the chlorides of oxygen-containing phosphorus acids react smoothly with aminoheterocycles in the presence of tertiary bases in non-polar and polar solvents and give rise to the corresponding amides in high yields. However, dialkyl phosphorochloridates do not react with 2-aminoquinoline in benzene; phosphorylation products have been obtained in 35% yield when the process was carried out in dioxan at 100 °C.[86] On reaction with dialkylphosphorochloridates, 2-aminopyridine *N*-oxide is converted into the corresponding hydrochloride[87].

It is noteworthy that dialkyl phosphorochloridates sometimes act as alkylating and not phosphorylating agents. Dimethyl phosphorochloridate reacts vigorously with 2-aminopyridine, the process being accompanied by a spontaneous temperature rise to 230 °C. *N*-Methylpyridone imine was isolated from the reaction products[100].

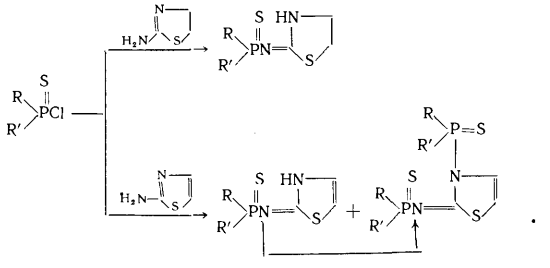
When 2-aminoquinoline *N*-oxide reacts with dialkyl phosphorochloridates, the products of its alkylation at the exocyclic nitrogen atom are formed[86].

The decrease of reactivity on passing from diaryl phosphorochloridates and diaryl phosphorochloridothioates to the chloride of dimethylphosphinothionic acid, caused by the decrease of electron density at the phosphorus atom, can be followed in relation to the reaction of 2-aminopyridine with phosphorus acid chlorides. For example, 2-aminopyridine reacts smoothly with diaryl phosphorochloridates and phosphorochloridothioates in benzene or toluene in the presence of tertiary bases[29]; the yields reach 60%. Aryl *N*-(2-pyridyl)methylphosphonoamidates and *N*-(2-pyridyl)-methylphosphonoamidothioates have been obtained in 40–70% yield on refluxing of the components in benzene for several hours[84]. Under these conditions, ethyl methylphosphonothioate was isolated in a yield less than 20%,[84] and, when the reaction of the chloride of dimethylphosphinothionic acid with 2-aminopyrimidine was carried out in moist benzene, only tetramethyl pyrophosphinodithioate was isolated[85]. However, when anhydrous pyridine is used as the solvent, thiophosphorylation of 2-aminopyridine (and also 2-aminopyrimidine, 2-aminothiazole, and 2-aminobenzothiazole) leads to dimethylthiophosphorylaminoheterocycles in yields of 60–70%.[85]

In the general case highly basic aromatic aminoheterocycles and heterocyclic imino-compounds substitute chlorine relatively readily in the chlorides of phosphoric, phosphonic, and phosphinic acids and also their thio-analogues when the reactions are carried out in both non-polar and polar solvents. Heteroaromatic compounds of the type of 2-aminopyridine and 2-aminopyrimidine react poorly or not at all in the required manner. The transition from non-polar to polar solvents sometimes leads to an increase of the reactivity of the initial components and the formation of phosphoryl- or thiophosphoryl-aminoheterocycles[85,86].

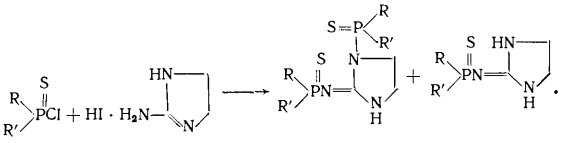
In the study of the reactions of aminoheterocycles containing the amidine system with the chlorides of oxygen- and sulphur-containing phosphorus acids it was noted that, depending on the phosphorylating agent, mono- or diphosphorylated products are formed[79]. The reactions with the chlorides of phosphonic acids result in the formation of

only 2 phosphorylamino-derivatives in all cases. The reactions with the chlorides of the sulphur-containing phosphorus acids proceed specifically as a function of the nature of the amine. 2-Aminothiazoline reacts with the chlorides of phosphonothioic acids to form the products of thiophosphorylation at the exocyclic nitrogen atom, while the reaction with 2-aminothiazole yields a mixture of products of thiophosphorylation at the exocyclic nitrogen atom alone and at both nitrogen atoms:



The diphosphorylation product is apparently obtained as a result of the stepwise substitution of the hydrogen atoms of the amino-groups by the phosphonothioic acid residue.

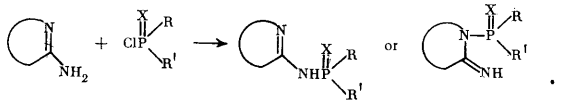
The reaction of equimolar amounts of 2-aminoimidazoline hydriodide with the chlorides of phosphonothioic acids in the presence of 2 moles of triethylamine led to the isolation of the products of diphosphorylation of 2-aminoimidazoline in 20% yield. The reaction of 3 moles of phenyl methylphosphonochloridothioate with 1 mole of 2-aminoimidazoline hydriodide leads to a mixture of di- and mono-phosphorylation products[79]:



The difference between the thiophosphorylation reactions is a consequence of the decrease of the nucleophilicity of the ring nitrogen atom in the series of thiophosphorylated 2-aminoimidazoline, 2-aminothiazole, and 2-aminothiazoline[79]. The absence of diphosphorylation products in the series of phosphonic acids can be explained not only by the decrease of the electron density at the endocyclic nitrogen atom in phosphorylaminoheterocycles compared with their thiophosphoryl analogues, as a consequence of the greater electron-accepting influence of the phosphoryl group, but also by the presence of a strong intramolecular bond between the phosphoryl oxygen and the hydrogen atom at the ring nitrogen atom.

The reaction of 3,5-diamino-1,2,4-thiadiazole or its salt with the chlorides of phosphorus acids leads to the formation of the products of the phosphorylation of only one amino-group[49].

Aminoheterocycles containing the amidine fragment N = C–N, in which one of the nitrogen atoms is exocyclic, can be phosphorylated at both endocyclic and exocyclic nitrogen atoms:



Furthermore, 2-phosphoryl(thiophosphoryl)amino-1-azaheterocycles can exist in the amino- or imino-forms:

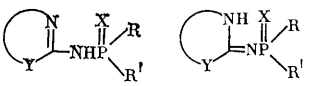


amino imino

In the determination of the structures of phosphoryl-(thiophosphoryl)aminoheterocycles, various spectroscopic methods were used for each group of compounds: ultraviolet and infrared spectroscopy and ^1H and ^{13}C NMR.[79,84,89,99,105]. Compounds with a fixed structure were used as standards. ^{31}P NMR could not be used for these purposes because of the complex dependence of the chemical shifts of the signals and their form on the immediate environment of the phosphorus atom[101]. It follows from the results that in all the cases investigated the phosphorylation (thiophosphorylation) of 2-amino-1-azaheterocycles involves the exocyclic nitrogen atom[79,84,89,99], except for derivatives of 3-amino-1,2,4-triazole[102–104].

The existence of a phosphorylated (thiophosphorylated) heterocyclic amine in the amino- or imino-form depends significantly on both the nature of the heterocycle and on the electron-accepting properties of the phosphorus-containing residue. Phosphorylated and thiophosphorylated aromatic aminoheterocycles, namely pyridine[84] and pyrimidine[89], exist exclusively in the amino-form regardless of the nature of the solvent and the phosphorus-containing residue. For derivatives of 2-aminobenzimidazoles and 2-aminobenzothiazole[99], whose aromaticity is lower, the influence of the phosphorus-containing residue is decisive. Phosphoryl derivatives exist in the imino-form, while thiophosphoryl derivatives exist in the amino-form. 2-Aminobenzoxazole[99], 2-amino-1-methylbenzimidazole[99], and 2-aminothiazole[79] are still less aromatic and their derivatives have the imino-structure. Phosphorylated 2-aminoaza-heterocycles, whose rings are not stabilised to some extent as a result of aromaticity, exist only in the imino-form[79] (see Table).

The structure of phosphorylated and thiophosphorylated 2-amino-1-azaheterocycles.

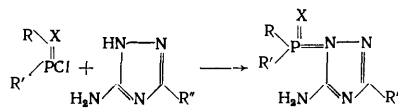


amino (A), imino (I)

Initial aminoheterocycle	X		Method of investigation	References
	O	S		
2-Aminopyridine	(A)	(A)	u.v.	84, 105
4-Aminopyridine	(A)	(A)	u.v.	84, 105
2-Aminopyrimidine	(A)	(A)	u.v.	105, 89
2-Aminothiazole	(I)	(I)	^1H NMR	105, 79
2-Aminobenzimidazole	(I)	(A)	u.v., i.r.	99
2-Aminobenzothiazole	(I)	(A)	u.v., i.r.	99
2-Aminobenzoxazole	(I)	(I)	u.v., i.r.	99
2-Amino-1-methylbenzothiazole	(I)	(I)	u.v., i.r.	99
2-Aminoimidazoline	(I)	(I)	^1H NMR	79
2-Aminothiazoline	(I)	(I)	^1H NMR	79

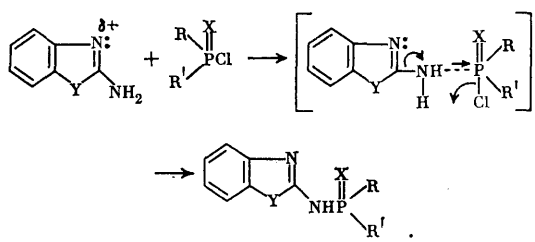
Prototropic tautomerism in these compounds has not so far been observed. We may also mention an NMR study of the diastereoisomers of phosphorylimino-oxazolidines[106].

The phosphorylation of 5-substituted 3-amino-1,2,4-triazole with phosphorus acid chlorides of different structure (including phosphoryl chloride) involves the nitrogen atom of the heterocycle in the 2-position[2-4,7,8,21,102-104,107-111]:



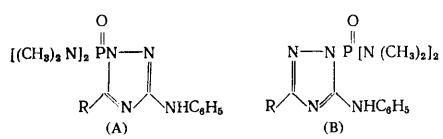
The structure of 1-phosphorylamino-derivatives, attributed by some workers to the phosphorylation products of 2-aminobenzimidazole[109], 5-aminotetrazole[110], and 4-amino-3,5-dimethylpyrazole, is either correct (cf. Grapov et al.[99]) or is insufficiently well founded.

According to quantum-mechanical calculations, the electron density maximum in heterocyclic amines containing the N = C–NH_2 group is located at the endocyclic nitrogen atom[112,113]. To account for the phosphorylation of the majority of such amines at the exocyclic nitrogen atom, one can postulate, in conformity with Katritzky's ideas[113], that heterocyclic amines react with acid halides in the tautomeric imino-form at the "hard" exocyclic nitrogen atom. The hypothesis that the polarisability of the aminoheterocycle molecule has an influence appears more probable. Under the influence of the phosphinyl (phosphinothionyl) group, the aminoheterocycle molecule is polarised and the electron could undergo a redistribution, which leads to an increase of electron density at the exocyclic nitrogen atom, which is then attacked by the phosphorus atom[99]:

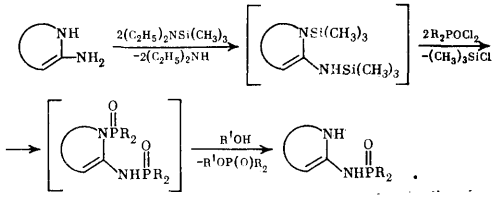


However, one cannot rule out the possibility of the initial attack by the phosphorus atom on the endocyclic nitrogen atom and subsequent migration of the phosphoryl group to the exocyclic nitrogen atom (cf. Simonov and Anisimova[114]).

Only isolated data are available for the reactions of 2-alkylamino- and 2-arylamino-heterocycles with phosphorus acid chlorides. When 2-methylaminobenzothiazole was allowed to react with phenyl methylphosphonochloridothioate, the product of thiophosphorylation at the exocyclic nitrogen atom was obtained[99]. 5-Alkyl-3-anilino-1,2,4-triazoles react with *N,N*-dimethylphosphoramidochloridate to form products of phosphorylation at the nitrogen atoms in both 2- and 1-positions, the product ratio being A : B = 2 : 13.[111]



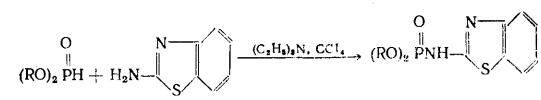
The method of phosphorylating 2-aminobenzimidazole, 3-amino-1,2,4-triazole, 2-aminobenzothiazole, and 2-aminopyrimidine with phosphorus acid chlorides using the trimethylsilyl protecting group is of interest[115]. When aminoheterocycles are treated with two equivalents of trimethylsilyldiethylamine, 1-trimethylsilyl-2-trimethylsilylaminoheterocycles are formed (except for 2-aminobenzothiazole, which reacts with only one equivalent of silylamine). When the reaction mass is treated with 2 moles of the acid chloride, the subsequent decomposition of the resulting 1-phosphoryl-2-phosphorylaminoheterocycles with alcohol results in the formation of 2-phosphorylaminoheterocycles:



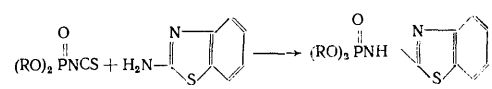
Although this method does provide for the consumption of twice the amount of the acid chloride, it makes it possible to obtain products which are known to be phosphorylated at the exocyclic nitrogen atom, including 3-phosphorylamino-1,2,4-triazoles, which cannot be obtained by the direct phosphorylation of 3-amino-1,2,4-triazole with phosphorus acid chlorides; however, we believe that this requires additional evidence.

2. Phosphorylation by Various Tetracoordinate Phosphorus Derivatives

A convenient method of synthesising phosphorylated aminoheterocycles is provided by the Todd–Atherton reaction. When acid phosphites or phosphonites were allowed to react with 2-aminobenzothiazole[116], 2-aminothiazole, and 2-aminothiazoline[79], the corresponding phosphorylated derivatives were obtained:

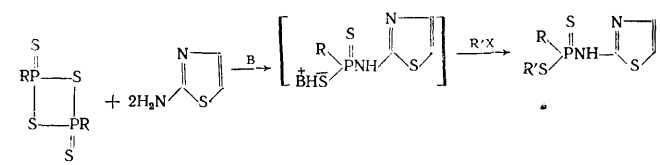


The isothiocyanates of phosphorus acids can also be used as phosphorylating agents. Levchenko and Sheinkman[117] showed for the first time that the reaction of diethyl and diphenyl phosphoroisothiocyanatidates with 2-aminobenzothiazole results in the formation of the corresponding 2-phosphorylaminobenzothiazoles:



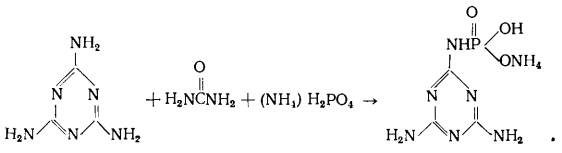
Methylphosphonoisothiocyanatidothioates react analogously with 2-aminothiazole and 2-aminothiazoline[79]. The isothiocyanate group then reacts as a pseudohalogen.

Dithiophosphorylaminothiazoles and aminopyridines have been obtained by the phosphorylation of the corresponding aminoheterocycles with dithioanhydrides of phosphonic acid, or more precisely with diphosphadithietans, and subsequent alkylation[42,45,118]:



Phosphate salts can also be used as phosphorylating agents. The monoammonium salt of 4,6-diamino-2-dihydroxyphosphorylamino-*sym*-triazine has been obtained by heating a mixture of ammonium dihydrogen phosphate, urea, and

melamine at 170–200 °C:[51]



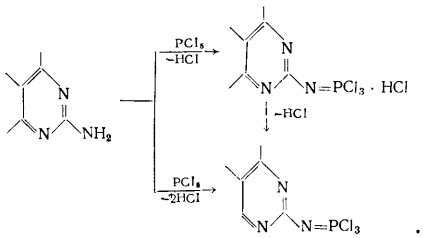
3. Phosphorylation with Phosphorus Pentachloride

One of the general methods of synthesising phosphorylated aminoheterocycles is the Kirsanov or phosphazo-reaction, an interaction of primary amines, in the given instance aminoheterocycles, with phosphorus pentachloride of halogenophosphoranes. 2-Aminopyridines[119], 4-aminopyridines[120], 2-aminopyrimidines[9,11,61,74,76,121], 4-aminopyrimidines[75,122], aminopurines[13], 3-aminobenzoisothiazole 1,1-dioxide[123], and aminotriazines[124,125] have been made to undergo this reaction.

The reactions of aminoheterocycles with phosphorus pentachloride are usually carried out in a boiling solvent (benzene, dichloroethane, and chlorobenzene).

It has been shown for 2- and 4-aminopyrimidines that, when the basicity of the initial aminopyrimidine is relatively low ($pK_a \leq 3.62$ for substituted 2-aminopyrimidines[76] and $pK_a \leq 3.7$ for 4-aminopyrimidines[75]), then two equivalents of hydrogen chloride are evolved in the reaction[75] and monomeric phosphazo-compounds are formed.

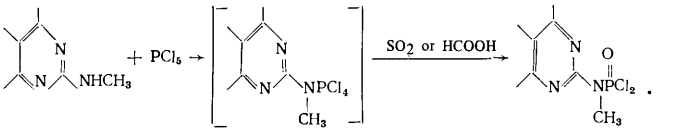
If the pK_a of the initial aminopyrimidines are greater than 3.62 for the 2-amino-derivatives and greater than 5.19 for the 4-amino-derivatives, then only one equivalent of hydrogen chloride is evolved and the hydrochlorides of phosphazopyrimidines are formed (the structure of pyrimidylaminophosphorus tetrachlorides was attributed to them previously[121]); on refluxing in chlorobenzene, one equivalent of hydrogen chloride is split off and the hydrochlorides are converted into monomeric phosphazo-compounds[75]. In contrast to heteroarylaminophosphorus tetrachloride derivatives, the hydrochlorides of phosphazoheterocycles do not react with anhydrous sulphur dioxide[75,76].



[^{32}P]Phosphazopyrimidines can be obtained by the same method[11].

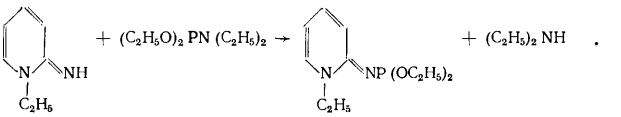
With increase of the number of amino-groups in amino-*sym*-triazines, the rate of the phosphazo-reaction diminishes[124]. The reaction of 2-amino-4,6-dichlorotriazine with 1 mole of PCl_5 terminates after 30 min and that of 2,4-diamino-6-chlorotriazine with 2 moles of PCl_5 terminates after 2–3 h, while the reaction of melamine with 3 moles of PCl_5 terminates after 5 h in dichloroethane and after 3–4 h in phosphoryl chloride.

On treatment with phosphorus pentachloride, 2- and 4-methylaminopyrimidines are converted into *N*-methyl-*N*-pyrimidinylaminophosphorus tetrachlorides, whose structure has been established by conversion into the corresponding acid dichlorides on treatment with sulphur dioxide or formic acid[74–76]:

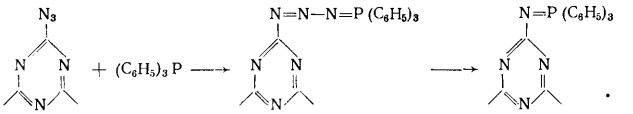


4. Phosphorylation with Tervalent Phosphorus Derivatives

When aminoheterocycles are phosphorylated with tervalent phosphorus derivatives, the reaction can proceed both without a change in valence and with formation of derivatives of tetracoordinate phosphorus. The transamidation of diethyl *N*,*N*-diethylphosphoramidite with 1-ethyl-2-pyridone imine yielded the corresponding phosphoramidite[126]:

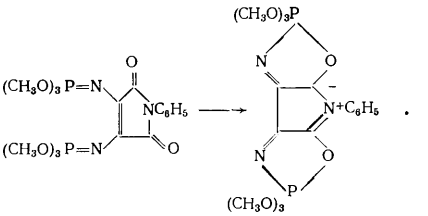


When heterocyclic azides are treated with tertiary phosphines or fully esterified phosphites, phosphazo-compounds are formed in high yields; in many instances it is possible to isolate the intermediate phosphazines. 4-Azido-5-chloro-1-phenyl-1*H*-pyridazin-6-one[127], 4-azidopyrrolin-2-ones[128], azido-*sym*-triazines[129,130], 9-azido-1,2,3,4-tetrafluoroacridine[131], 4-azido-5*H*-furan-2-ones[128], diazidopyrroline-2,5-dione[132], 2-azido-3-ethylbenzothiazolinium fluoroborate[126], and 3-azido-1-ethylpyridinium fluoroborate[126] have been made to undergo this reaction. The reaction is carried out by allowing the azides of the heterocycles to interact with triphenylphosphine in an organic solvent (methylene chloride, ether):



In the reaction of azidotriazines with trialkylphosphites at 5–10 °C it was possible to isolate the intermediate phosphazidotriazines, which split off a nitrogen molecule on heating and are converted into phosphazotriazines[129].

3,4-Diazidopyrroline-2,5-dione reacts with 2 moles of trimethyl phosphite to form the stable 3,4-bisphosphazopyrroline-2,5-dione. The authors explain its stability[132] by the fact that it exists in the form of a dipolar ion:

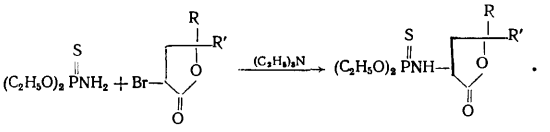


5. Phosphorylamidation Reactions

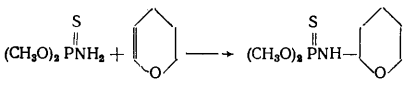
Whereas the methods for the phosphorylation of aminoheterocycles are general for the synthesis of various derivatives of this class, the phosphorylamidation and cyclisation methods are to a large extent specific and can

be used only for the synthesis of a small group of compounds of similar structure.

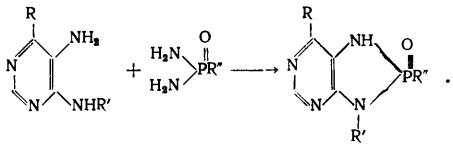
A small group of methods for the synthesis of phosphorylaminoheterocycles is based on the reaction of phosphorus acid amides with different derivatives of the heterocycles. When 3-halogenolactones are heated with diethyl phosphoramidothioate in the presence of triethylamine, the corresponding derivative of 3-aminohydrofuran-2-one is formed[133]:



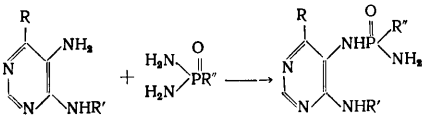
O,O-Dimethyl and *O,S*-dimethyl phosphoramidothioates add to dihydropyran in the presence of catalytic amounts of toluene-*p*-sulphonic acid[30]:



The condensation of phosphonodiamidates with 4,5-diaminopyrimidines usually results in the formation of 1,3-diaza-1,3-dihydro-2-phospholo[4,5-*d*]pyrimidines[134,135]:

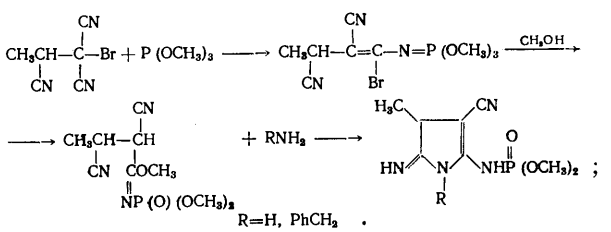


In certain cases only one amino-group, in the 5-position, is involved in the reaction and 4-amino-5-phosphorylaminopyrimidines are formed[135]:

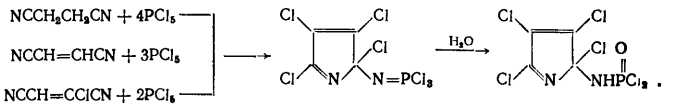


6. Cyclisation Reactions

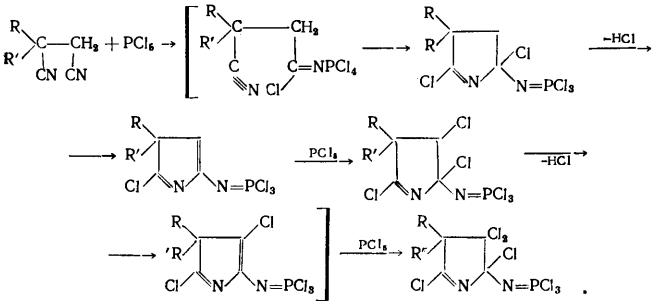
(*a*) *Derivatives of five-membered aminoheterocycles with one heteroatom.* The phosphorylated derivatives of aminopyrroline are obtained from di- and tri-nitriles. When α-bromo-α,α,β-tricyanopropane is treated with trimethyl phosphite, the corresponding iminotrimethoxyphosphorane is obtained and on treatment with methanol is converted into an *N*-methylenephosphonamidate. On treatment with benzylamine or ammonia, the latter is converted into a substituted 2-dimethoxyphosphorylamino-Δ^2-pyrroline[136]:



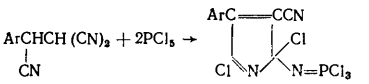
The dinitriles of unsubstituted, monosubstituted, and disubstituted succinic acid as well as the dinitriles of maleic, fumaric, and chloromaleic acids react with phosphorus pentachloride to form 2-trichlorophosphazopolyhalogenopyrrolenines. On controlled hydrolysis, the latter are readily converted into dichlorophosphorylaminopolyhalogenopyrrolenines[137–140]:



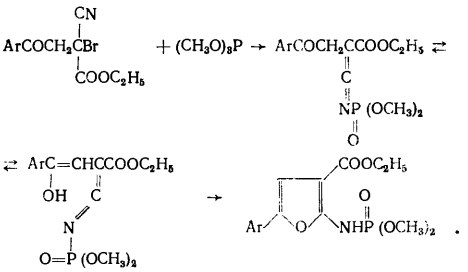
The presence of substituents in the α-position in the dinitriles of succinic acid does not prevent their cyclisation. Since nitriles not containing a hydrogen atom in the α-position do not react with phosphorus pentachloride, the following mechanism of the cyclisation reaction has been proposed[139]:



The reaction begins with the addition of phosphorus pentachloride to the cyano-group at the primary carbon atom. 2-Aryl-1,1,2-tricyanoethanes react via a similar mechanism[141]:

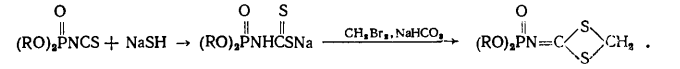


Substituted aminofurans are formed when ethyl α-bromo-α-cyano-β-benzoylpropionate is treated with trimethyl phosphite[142]:

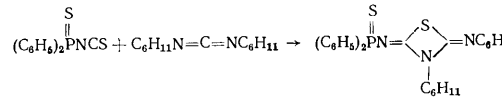


The authors[142] postulated the formation of a keten imine as an intermediate.

(*b*) *Derivatives of four- and five-membered aminoheterocycles with two heteroatoms.* *N*-Phosphorylated 2-amino-1,3-dithietans are obtained by the cyclisation of the sodium salts of *N*-phosphoryldithiocarbamic acids, which are formed when sodium hydrogen sulphide reacts with phosphoroisothiocyanatidates; the cyclisation takes place on treatment with methylene bromide in the presence of sodium dicarbonate[31–34]:

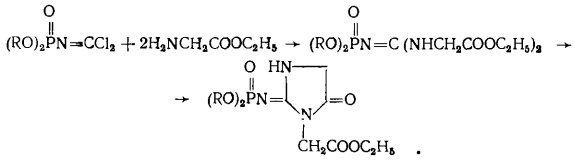


When diphenylphosphinothionyl isothiocyanate is heated with dicyclohexylcarbodi-imide, a 1,2-cycloaddition reaction takes place and a 1,3-thia-azetidine derivative is formed[143]:

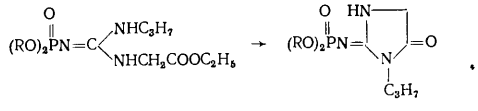


Thus it has been shown that the cycloaddition of isothiocyanates with electron-accepting groups to carbodi-imides takes place at the C–S- and not the C = N bond.

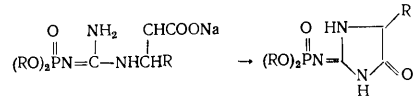
The method of synthesis of phosphorylated imino-imidazolidinones from dichloro-methyleneamides of phosphorus acids is of interest[144]. The reaction of *N*-dichloromethylene-phosphoramidate with ethyl glycinate results in the formation of the corresponding substituted guanidine, which splits off an alcohol molecule on distillation and is converted into a derivative of phosphoryliminoimidazolidinone:



Phosphorylated 1-alkyl-2-iminoimidazolidinones are synthesised via an analogous mechanism involving the thermal decomposition (*in vacuo* at 80–120 °C) of *N*-ethoxycarbonyl-methyl-*N'*-propyl-*N''*-diethoxyphosphinylguanidine[145,146]:

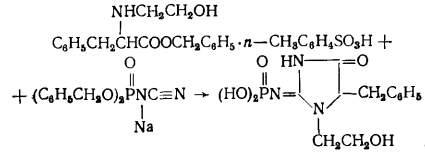


Yet another method of synthesis of phosphorylated imidazolidines consists in the cyclisation of derivatives of *N*-α-carboxyalkyl-*N'*-phosphorylguanidine. The latter are obtained by heating phosphoryl-*N*-methylisothiourea with mercury(II) oxide and subsequent treatment with aminoacids or their derivatives[147,148]:

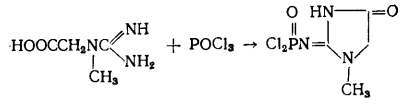


When the disodium salt of *N*-(1,2-dicarboxyethyl)-*N'*-phosphorylguanidine is reduced with hydrogen (on the Pd/C catalyst), 5-ethyl-2-phosphoryliminoimidazolidin-4-one is obtained[147].

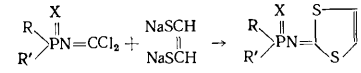
The condensation of the tosylates of the esters of *N*-β-hydroxyalkylaminoacids with salts of phosphorylated cyanamides followed by hydrolysis results in the formation of 1-(β-hydroxyethyl)-2-phosphoryliminoimidazolidin-4-ones[149]:



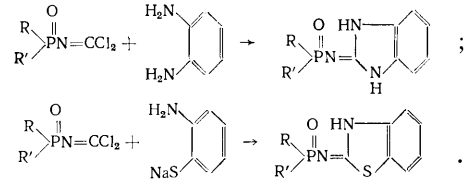
When creatine is refluxed with an excess of phosphoryl chloride, dichlorophosphorylcreatinine is formed[150]:



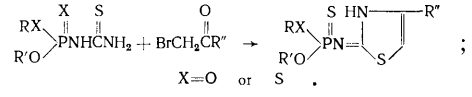
Derivatives of iminodithiole are obtained by the reaction of dialkyl *N*-dihalogenomethylenephosphoramidates with the disodium salt of *cis*-1,2-dimercaptoethylene[91]:



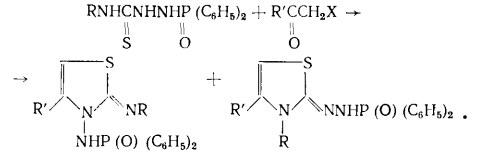
Derivatives of phosphorylaminobenzimidazole and phosphoryl-aminobenzothiazole have been obtained analogously from *N*-dichloromethylenephosphoramidates or *N*-dichloromethylene-phosphonamidates and a diamine of the sodium salt of *o*-aminothiophenol[99]:



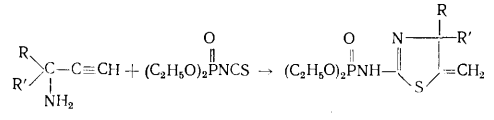
A method of synthesis of aminothiazoline derivatives, consisting in the reaction of thio- or dithio-phosphoryl-thioureas with α-halogenoketones, has been developed[48]:



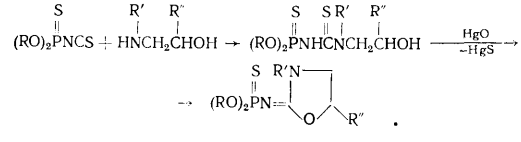
When α-halogenoketones were allowed to react with diphenylphosphorylthiosemicarbazide, mixtures containing 2-alkylimino-3-phosphorylamino-1,3-thiazolines and phosphorylated 2-hydrazino-1,3-thiazolines were obtained[151]:



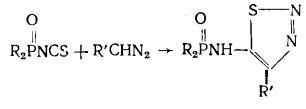
The reaction of diethyl phosphoroisothiocyanatidates with α-aminoacetylenic derivatives takes place vigorously and results in the formation of diethoxyphosphorylamino-thiazoline having a methylene substituent in the 5-position[152]:



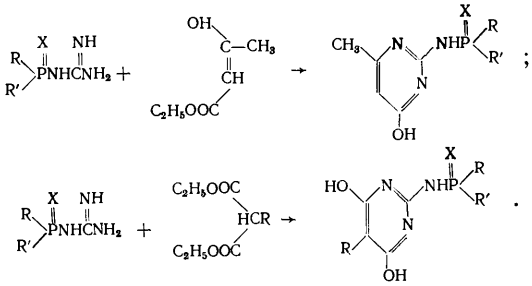
Phosphorylated 2-imino-oxazolidines are obtained by the reaction of the isothiocyanates of phosphorus thioacids with *N*-alkylethanolamines followed by the elimination of hydrogen sulphide from the resulting phosphorylated urea under the influence of mercury(II) oxide[38,40,41,82,96,153]:



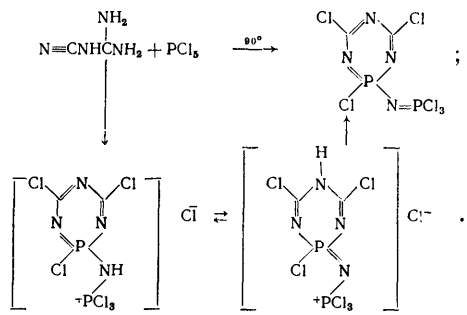
Phosphinyl isothiocyanates react with aliphatic diazo-compounds via the 1,3-dipolar cycloaddition mechanism and form 5-phosphorylamino-1,2,3-thiadiazoles[154]:



(*c*) *Derivatives of six-membered aminoheterocycles.* One of the possible ways of synthesising phosphorylated 2-aminopyrimidin-4-ones and 2-aminopyrimidine-2,6-diones may be the condensation of guanidinophosphoric acid with β-carbonyl compounds, for example with acetoacetic or malonic esters[89,155]:



The reaction of dicyanodiamide with phosphorus pentachloride leads to two compounds depending on the conditions[156]. When a 1:2 mixture of the components is heated at 90 °C for 4–5 h, 1,3,5-trichloro-1-trichlorophosphazo-1-phospha-2,4,6-triazine is formed. On the other hand, if the reaction is carried out in dichloroethane at 35 °C, it is possible to detect the formation of an intermediate salt-like product which splits off hydrogen chloride on being refluxed in dichloroethane and is converted into a phosphazo-compound:



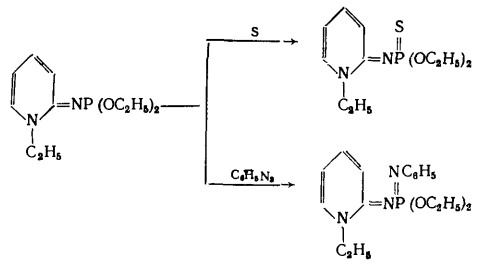
III. REACTIONS OF PHOSPHORYLATED AND THIOPHOSPHORYLATED AMINOHETEROCYCLES

Phosphorus-containing aminoheterocycles, obtained by the methods described in the previous sections, can undergo in many instances addition, substitution, oxidation, reduction, etc. reactions, forming new derivatives of phosphorylaminoheterocycles with a different environment at the phosphorus atom or with new substituents in the heterocyclic ring.

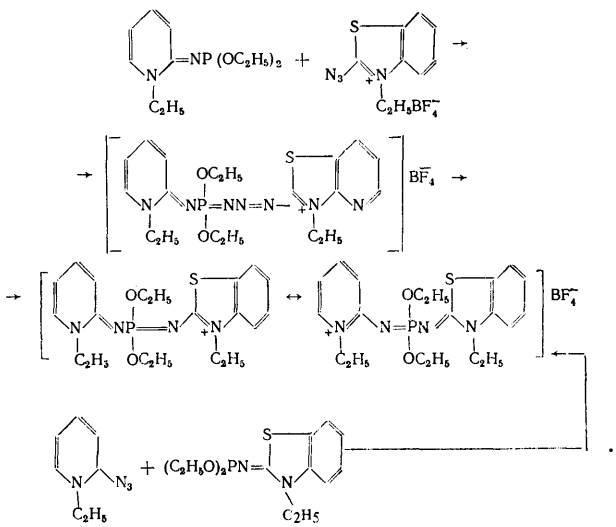
1. Reactions of Tervalent Phosphorus Derivatives

Phosphorylated aminoheterocycles, containing a tervalent phosphorus atom, enter into reactions characteristic also of other tervalent phosphorus derivatives.

Diethyl *N*-(1-ethyl-1,2-dihydropyridylidene)phosphoramidite readily combines with sulphur or phenyl azide and forms the corresponding phosphoramidothionate or iminophosphorane[126]:



The phosphorus analogues of carbocyanines have been obtained by the same procedure[126]. When diethyl imidophosphite *N*-(1-ethyl-1,2-dihydro-2-pyridylidene)-phosphonamidite reacts with 2-azido-1-ethylbenzothiazolium fluoroborate in chloroform at 20 °C, the product is a phosphatriazene, which decomposes on heating in chlorobenzene to form a phosphacyanine. The same phosphacyanine has been obtained by the reaction of 2-azido-1-ethylpyridinium fluoroborate with the corresponding phosphoramidite:

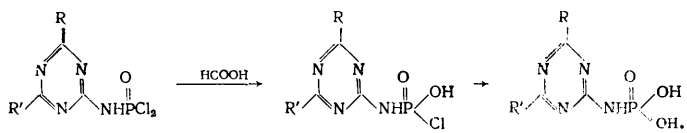


The results show that the positive charge is delocalised over the terminal nitrogen atoms in the phosphacyanine formed.

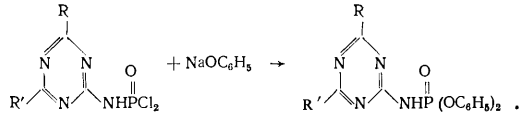
2. Reactions of Tetracoordinate Phosphorus Derivatives

Phosphorylaminoheterocycles can undergo reactions accompanied by a change in the environment at the phosphorus atom or in the heterocyclic ring and also with the dissociation of the nitrogen–phosphorus bond.

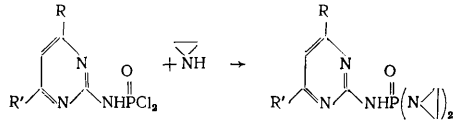
(*a*) *Nucleophilic substitution reactions of dichlorophosphorylaminoheterocycles.* Dichlorophosphorylaminoheterocycles readily react with various nucleophiles: water, acids, alcohols, phenols, and amines. Controlled hydrolysis of dichlorophosphorylaminotriazines has been achieved[124] by treatment with anhydrous formic acid:



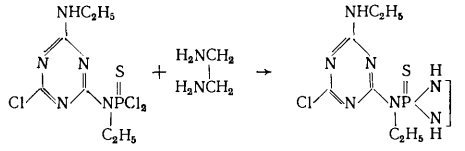
Dichlorophosphorylaminoheterocycles readily react with alcohols[157] and phenoxides[120,123,157], forming the corresponding ester-amides:



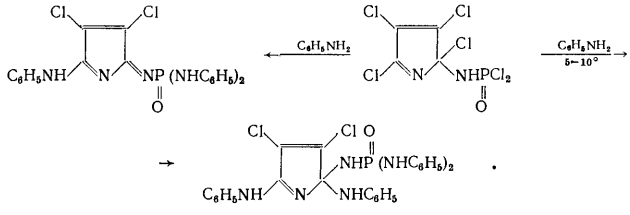
They also readily react with ammonia[23,25,73,78], primary[123] and secondary[103] aliphatic amines, anilines[123,157], piperidine[76], and morpholine[61,76]. This method has acquired particular importance for the synthesis of aziridinyl phosphates with carcinolytic activity[9,11–19,60–66,68,69,158,159]:



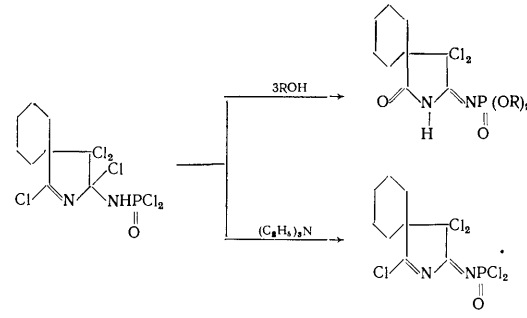
The hydrochloride of dichlorophosphorylaminopyrimidine can also be introduced into the reaction[75]. When 6-chloro-2-(*N*-dichlorothiophosphoryl-*N*-ethylamino)-4-ethylamino-*sym*-triazine reacted with ethylenediamine, the corresponding triazinylaminodiazaphospholane was obtained[26]:



The aminolysis and alcoholysis of dichlorophosphorylaminoperchloropyrrolenines and pyrrolines do not proceed via the standard mechanism. When the dichloride of *N*-perchloropyrroleninylphosphoramidic acid is treated with aniline in boiling benzene, hydrogen chloride is split off and at the same time both the chlorine atoms of the acid chloride groups and that in the 2-position are substituted; the reaction with aniline at 5–10 °C results in the substitution of four chlorine atoms[139]:

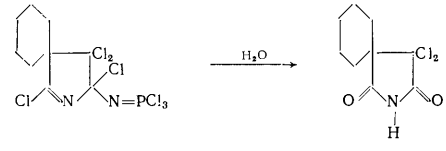


When the dichloride of 2,4,4,5-tetrachloro-3,3-pentamethylene-5-pyrrolinylphosphoramidic acid interacts with three equivalents of alcohol the chlorine atoms in the 2- and 5-positions in the pyrroline ring react, apart from the chlorine atoms attached to the phosphorus atoms[138,139,160]. When the same dichloride was treated with triethylamine, the 2,4,4-trichloro-derivative was obtained[139]:

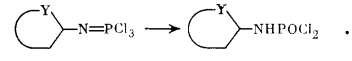


(*b*) *Nucleophilic substitution reactions of trichlorophosphazoheterocycles.* Trichlorophosphazoheterocycles also readily react with various nucleophiles. They rapidly hydrolyse under the influence of atmospheric moisture and cold water with cleavage of the nitrogen–phosphorus bond and the formation of hydrogen chloride, phosphoric acid, and the initial aminoheterocycles[123,139–141].

2,4,4,5-Tetrachloro-5-trichlorophosphazo-3,3-pentamethylenepyrroline is hydrolysed by water to the corresponding succinic acid amide[139]:

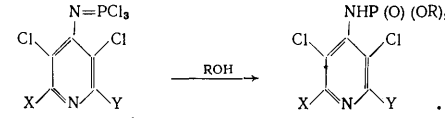


The acidolysis of trichlorophosphazoheterocycles by formic[74,75,120–122,124,141,146] or acetic[11,75,122,123,139,140] acids results in the formation of dichlorophosphorylaminoheterocycles:



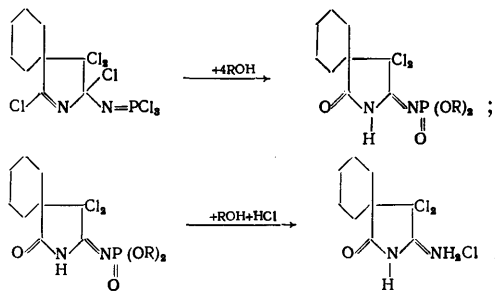
4-Trichlorophosphazopyrimidine reacts with glacial acetic acid to form dichlorophosphorylaminopyrimidine, while the reaction with anhydrous formic acid results in the corresponding hydrochloride[75].

On treatment with alcohols, not only are chlorine atoms substituted but also a rearrangement of the type of the second stage of the Arbuzov reactions takes place and the diesters of *N*-heterylphosphoramidic acid are formed[120,140,157]:

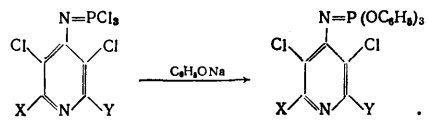


The interaction of 2,4,4,5-tetrachloro-2-trichlorophosphazopyrroline with four moles of alcohol in benzene at 80 °C or in carbon tetrachloride for 20–30 min involves not only the chlorine atoms of the phosphazo-group but also the chlorine atoms in the 2- and 5-positions of the pyrroline ring with formation of the esters of 3,3-dichloro-5-oxo-2-pyrrolidinylidenephosphonamidic acid[138,139,160]. If this reaction is carried out in a large excess of boiling alcohol without a solvent but in the presence of hydrochloric acid,

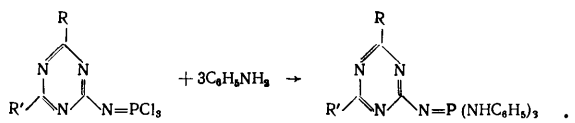
the P–N bond is ruptured[138,139,160]:



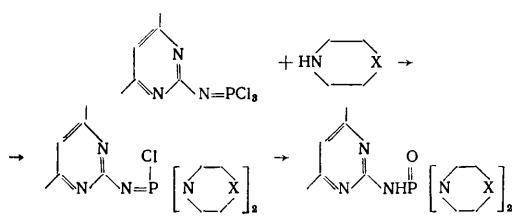
Trichlorophosphazo-derivatives also readily react with alkali metal phenoxides to form the corresponding triphenoxyiminophosphoranes[120,125,127]:



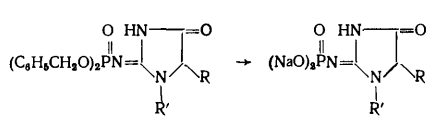
When phosphazoheterocycles are treated with amines, three chlorine atoms are as a rule substituted with formation of triaminoiminophosphoranes[125,140]:



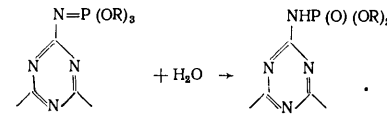
However, the reaction of 2- and 4-trichlorophosphazopyrimidines with morpholine and piperidine proceeds with substitution of only two chlorine atoms and the formation of diaminochloroiminophosphoranes[75,76,119,146], which are converted into phosphorotriamides on heating with 96% alcohol. The hydrochlorides of 2- and 4-trichlorophosphazopyrimidines react analogously[75,76].



(c) *Nucleophilic substitution reactions of other phosphorylaminoheterocycles.* The acid hydrolysis of phosphorylaminoheterocycles results in the rupture of the nitrogen-phosphorus bond and the liberation of the initial heterocycles[159]. The alkaline hydrolysis of dibenzyl *N*-heterylidenephosphoramidates involves the dissociation of the P–O bonds and the formation of alkali metal salts of *N*-heterylidenephosphoramidic acids[147,149,161]:

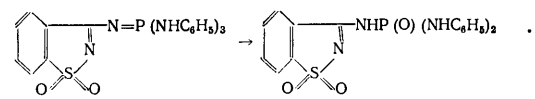


The kinetics of the hydrolysis of the dialkyl esters of phosphoryliminohydantoins have been studied[162]. The hydrolysis of triphenoxy- and trialkoxy-*N*-heterylidenephosphoranes results in the formation of the corresponding esters of phosphoramidic acid[29,120,125,129,157]:

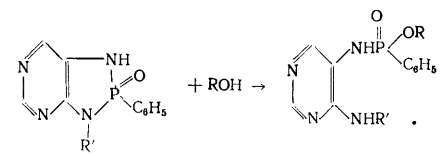


Under these conditions, triphenoxy-*N*-triazinyliminophosphoranes are stable—they do not hydrolyse on being refluxed with 1 *N* hydrochloric acid[130].

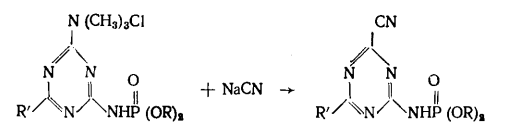
The trianilino-derivatives hydrolyse even on being refluxed in 96% alcohol and give rise to dianilinophosphorylaminoheterocycles[123]:



The diazaphosphole ring in 1,3-diaza-1,3-dihydro-2-phospholo[4,5-*d*]pyrimidine 2-oxide is readily cleaved at the P–N bond on treatment with water or alcohol; derivatives of 4-amino-5-phosphorylaminopyrimidine are formed[135]:



N-Phosphorylated derivatives of aminotriazines[22,27,163,164], aminopyrimidines[159], and aminoacridines[165], containing labile atoms or groups in the heterocyclic ring, readily exchange them under the influence of various nucleophiles. For example, (2-phosphorylamino-4-*sym*-triazinyl)trimethylammonium chloride is converted into the corresponding 4-cyano- or 4-azido-derivative under the influence of sodium cyanide[22]:

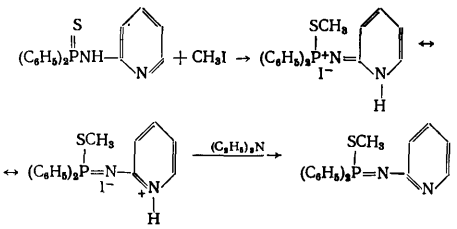


Polyfluoro-9-acridinyliminotriphenylphosphoranes react with alkoxides, phenoxides, and primary and secondary amines with substitution of only one fluorine atom[165].

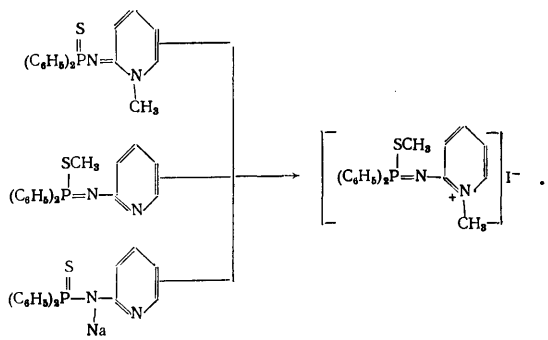
(d) *Electrophilic substitution reactions.* Interesting data have been obtained in the study of electrophilic substitution reactions involving phosphorylated and thiophosphorylated aminoheterocycles containing the amidine system.

Phosphorylaminoheterocycles do not undergo the electrophilic substitution reaction[166]. 2-Dimethylthiophosphorylamino-derivatives of pyridine, pyrimidine, and triazole are readily methylated by methyl iodide at the sulphur atom with dissociation of the P–S bond and are converted into phosphonium salts stabilised by resonance with the iminophosphorane structure[167]. 2-Diphenylaminothiophosphorylaminopyrimidine reacts with methyl iodide to form an adduct of a phosphonium salt with methyl iodide, from which a stable adduct of the phosphonium salt and benzene was obtained on treatment with an excess of benzene. The latter adduct is converted into the corresponding imino-

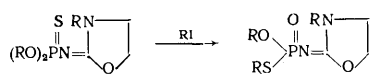
phosphorane on treatment with ammonia or triethylamine:



On being refluxed in benzene, the iminophosphorane isomerises to methyl *N*-(1,2-dihydro-2-pyridylidene)diphenylphosphinamidothiolate[167]. Its methylation as well as the methylation of methylthiodiphenyl-*N*-(2-pyridyl)iminophosphorane and the sodium salt of *N*-(2-pyridyl)diphenylphosphinamidothioate with methyl iodide in nitromethane leads to the same product:

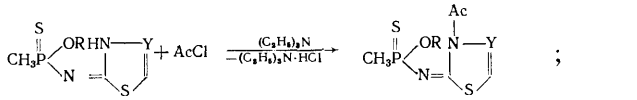


The attempts to methylate dialkoxyphosphoryl- and aryloxymethylthiophosphorylamino-derivatives of thiazoles, thiazolines, and thiadiazoles were unsuccessful[166]. On treatment with alkyl iodides, dialkoxythiophosphoryliminothiazolidines and the corresponding oxazolidines isomerise via the Pishchimuka reaction and give rise to the corresponding phosphoramidothiolates[38,153]:



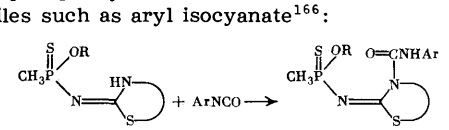
As a rule, 2-phosphorylaminoazaheterocycles are not protonated and do not form salts with acids. The picrates and nitroindandionates of phosphorylated 2-aminopyrimidines have been described[86].

Thiophosphorylated derivatives of 2-aminothiazole and 2-amino-1,3,4-thiadiazole react with the chlorides of phosphorus thioacids and benzenesulphonyl chloride to form products of substitution at the endocyclic nitrogen atom[166]:



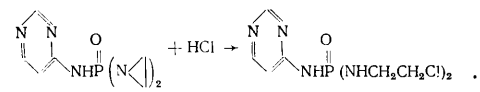
Y=N or CH; Ac=CH_3 (RO) P (S), or $C_6H_5SO_2$.

Under analogous conditions, thiophosphoryliminothiazolidines do not react. However, not only thiophosphorylated 2-aminothiazoles and 2-aminothiadiazoles, but also 2-thiophosphorylaminothiazolines react with hard electrophiles such as aryl isocyanate[166]:



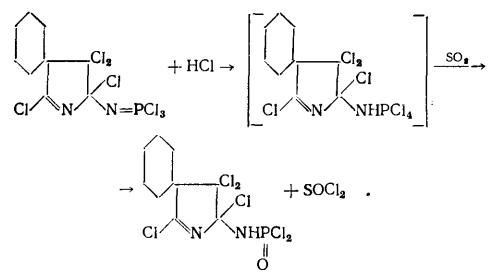
The greater ease of electrophilic substitution reactions for thiophosphorylated derivatives of aminothiazole and aminothiadiazole compared with the derivatives of aminothiazoline can be explained by the more pronounced nucleophilic properties of the endocyclic nitrogen atom in the thiophosphoryliminoheterocycles as a consequence of the electron-donating influence of the neighbouring π-bond.

(*e*) *Other reactions.* In many instances diaziridinoheteryl-aminophosphine oxides are converted by anhydrous hydrogen chloride into the corresponding bis(β-chloroethylamino)-derivatives in high yields[10,62]:

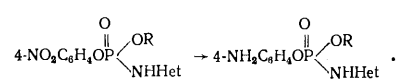


It has been noted[159] that, when diaziridino(4-chloropyrimidinyl-2-morpholinylamino)phosphine oxide is refluxed in dilute hydrochloric acid, a mixture of the hydrochloride of the initial pyrimidine and *N*,*N*'-bis(2-chloroethylamino)-pyrimidinylphosphonamidate is formed.

Trichlorophosphazoheterocycles readily combine with anhydrous hydrogen chloride at the P = N double bond and give rise to phosphorus tetrachloride derivatives. The latter are unstable and are converted under the influence of sulphur dioxide into the corresponding dichlorophosphorylated derivatives[139-141]:



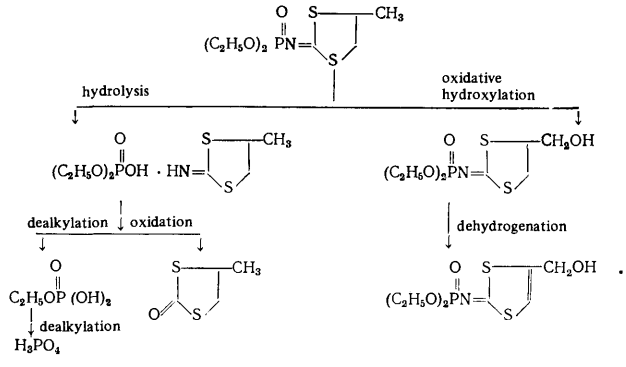
The amides of *p*-nitrophenylphosphonic acid, containing the heterocyclic residue at the nitrogen atom, are reduced with hydrogen in the presence of Raney nickel to the corresponding derivatives of *p*-aminophenylphosphonic acid[80,168]:



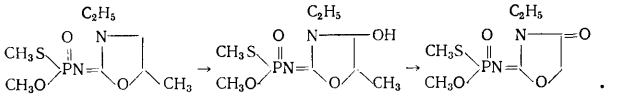
(*f*) *Reactions of phosphorylaminoheterocycles in the environment and in living organisms.* In connection with the high biological activity of certain phosphorylaminoheterocycles and their use as plant protecting agents, their photolysis and behaviour in living organisms have been investigated.

After the exposure of aqueous solutions of 2-diethoxyphosphorylimino-4-methyl-1,3-dithiolan to sunlight, its hydrolysis products were isolated: diethylphosphoric acid, monoethylphosphoric acid (in small amounts), and 2-imino-4-methyldithiolan[169]. The preparation decomposes via the same mechanism in paddy rice plants[170]. When a 2% aqueous solution of acetone was used as the solvent in the study of the photolysis of 2-diethoxyphosphorylimino-4-methyl-1,3-dithiolan, the main decomposition product was *S*,*S*-1,2-propylene dithiocarbonate[169].

The main process determining the metabolism of 2-diethoxyphosphorylimino-4-methyl-1,3-dithiolan in the cotton plant is oxidative hydroxylation of the methyl group in the 4-position with partial dehydrogenation of the molecule:



3-Ethyl-2-methoxymethylthiophosphorylimino-5-methyl-1,3-oxazolidine also undergoes oxidative phosphorylation in the cotton plant, in the organisms of house flies, and in enzymatic and model oxidation systems; the 4-hydroxy derivative is readily converted into the 4-oxo-derivatives[39]:



* * *

In conclusion one may note that, as shown by the data presented above, this interesting branch of chemistry, related, on the one hand, to the chemistry of organoelemental compounds and, on the other hand, to the chemistry of heterocycles, has been developing vigorously in recent years. The results permit one to hope that new physiologically active compounds of this class will be found in the immediate future and experimental data of theoretical value will be obtained.

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Polyphosphazens

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The main features of the catalytic and thermal polymerisation of chlorocylophosphazens are examined, with a possible mechanism of rearrangement of rings in the thermal polymerisation of mixtures of cyclic chlorophosphazens. Research on the influence of side-groups on the chemical and physicochemical properties of polyorganophosphazens (polydialkoxyphosphazens, polydiaminophosphazens) is discussed, as well as aspects of the vulcanisation and stabilisation of these polymers. The chemical properties, structure, molecular-mass characteristics, and thermal stability of polyphosphazens are surveyed, and also the application of these polymers in the national economy. A list of 151 references is included.

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I. INTRODUCTION

Interest in polyphosphazens has increased considerably during recent years, as a consequence of the undoubted practical value of this interesting class of hetero-organic polymers. The large quantity of experimental results and the many original investigations following publication of Allcock's monograph[1] and a review[2] have made it necessary to summarise some of the most important aspects of the chemistry of polyphosphazens. We have now attempted to systematise work appearing during recent years on the synthesis and properties of linear homopolyphosphazens, a most interesting and industrially important type of phosphazen polymers. The survey of published data has taken into account recent reviews[3-10], most of which cover only part of the field or are essentially advertising material.

II. POLYHALOGENOPHOSPHAZENS

The only method for synthesising linear macromolecular polyphosphazens has been to replace halogen atoms in polydihalogenophosphazens by various groups. Since polydichlorophosphazen is most often used for this purpose, establishment of the laws and mechanism of its formation in the polymerisation of chlorocyclophosphazens is a most urgent problem of phosphazen chemistry.

The polymerisation of cyclic chlorophosphazens

$$(PNCl_2)_n \xrightarrow{200-300^\circ} -\left[\begin{array}{c} Cl \\ | \\ -P=N- \\ | \\ Cl \end{array}\right]_x -$$

$n=3-8,\ x \lesssim 15\,000$

known long ago from the work of Stokes[11], can be accomplished either thermally or catalytically. Research during recent years on the catalytic polymerisation of hexachlorocyclotriphosphazen has determined the most effective range of catalysts for subsequent investigation. Alkali-metal phenoxides and alkoxides[12], inorganic acids, and hetero-organic Lewis acids (e.g. ethylaluminium halides)[13] enable the temperature to be lowered to 200 °C. Use of 1 mass % of phosphoric acid[17] also permits the above chlorocyclophosphazen to be polymerised in a solvent (1,2,4-trichlorobenzene) at this temperature; the resulting polydichlorophosphazen has a lower molecular mass and a broader distribution thereof than has that obtained purely thermally[7,14].

The use of metal chlorides[15], known some time ago for the splitting of chlorocyclophosphazens[16,17], enables the temperature of polymerisation to be lowered to 175–200 °C, but also leads to a decrease in molecular mass that is larger the greater the quantity of catalyst.

Ring opening occurs in hexachlorocyclotriphosphazen under mild conditions in the presence of phenylmagnesium bromide[18] or diphenylmagnesium[19], and especially readily (at 20 °C) on treatment with phenyl-lithium[20]. In the last case the first stage involves formation of a linear product $C_6H_5PCl_2NPCl_2$. $.NPCl_2NLi$, which undergoes further phenylation by excess of phenyl-lithium (mainly from the end), but in the presence of a deficiency of this compound branched structures are formed owing to interaction with other similar molecules, the resulting oligomer having molecular mass up to 2000 and relative composition

$$(C_6H_5)_3P : (C_6H_5)_2P : PCl_2 = 5 : 2 : 22.$$

Low-temperature opening of phosphazen rings is fundamentally possible[18-20], but the catalysts used must be inert towards phosphorus–chlorine bonds.

Since effective catalysts for the polymerisation of chlorocyclophosphazens have not yet been found, thermal polymerisation mainly of a cyclic trimer remains the chief method for obtaining polydichlorophosphazen. Despite the large amount of research on thermal polymerisation[1,2] methods are not yet available for conducting the process under controlled conditions, which would yield reproducible results; nor can the yield, solubility, and molecular-mass characteristics of the products be controlled.

It now seems highly likely that the usual thermal polymerisation of hexachlorocyclotriphosphazen and other chlorocyclophosphazens is not a truly thermal process, but is determined in considerable measure by the presence of impurities in the initial cyclic compound and on the walls of the reaction vessels. Thus hexachlorocyclotriphosphazen that has been thoroughly purified by successive recrystallisation, boiling with barium oxide in a stream of nitrogen at 130 °C, passage of the vapour over phosphorus pentoxide, and vacuum sublimation does not polymerise below 300 °C,[21] but rapid polymerisation begins after the introduction of oxygen. The reason for this and the nature of the active centres were not discussed[21]. An effective method for purifying the trimer is first to heat it under polymerisation conditions (200–250 °C) for 15–180 min and then distil[22]: polymerisation of the purified product gives a higher yield

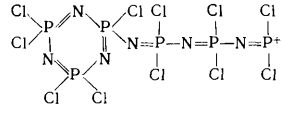
of soluble polydichlorophosphazen, but the rate of the process is lowered.

The now preferred ionisation mechanism of the thermal polymerisation of hexachlorocyclotriphosphazen[23-25] involves as initial stage heterolysis of a phosphorus–chlorine bond with formation of a cyclic azophosphonium cation

$$P_3N_3Cl_6 \rightleftarrows P_3N_3Cl_5^+ + Cl^-$$

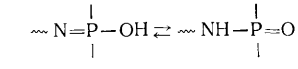
that initiates chain growth. It was confirmed in later work[26,27], and agrees well with conductivity measurements on the trimer and on polydichlorophosphazen[28].

Examination of the effects of pH at the surface of the glass ampoules, temperature, and duration[29], indicating an increase in the rate of polymerisation of hexachlorocyclotriphosphazen with increase in acidity of the glass, suggested in terms of the ionisation mechanism[26] that chain growth begins with protonation of a trimer molecule. The cation $P_3N_3Cl_6H^+$ then reacts with a second trimer molecule to eliminate hydrogen chloride and form the cyclolinear cation

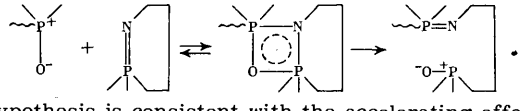


which is responsible for further chain growth, as in the usual ionisation polymerisation[26].

However, the hydrogen chloride not only does not catalyse polymerisation but is even capable of inhibiting it slightly[30]. Phosphorus pentachloride is a stronger inhibitor of this process, and also acts as a telogen[30,32]. The accelerating effect of small additions of water (10^{-5}–10^{-1} mole mole^{-1} trimer) also indicates that the main role in initiating polymerisation is played by acid centres of the type

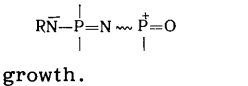


formed at the same time as hydrogen chloride[30,31]. Allcock's results[30] indicate that chain growth in the polymerisation of chlorocyclophosphazens is effected not only by an azophosphonium cation but also by a terminal phosphoryl group:



(1)

This hypothesis is consistent with the accelerating effect of phosphoric acid[17] and alkoxy-derivatives of the trimer[12] on its polymerisation; it is assumed in the latter case that phosphazen–phosphazan rearrangement takes place, and the resulting phosphazan is converted into a zwitterion



which initiates chain growth.

Although formation of cationic centres seems to be generally accepted as initiating chain growth in the thermal polymerisation of hexachlorocyclotriphosphazen, information on the laws of chain growth and termination has hitherto been almost completely lacking, and the reasons for the wide molecular-mass distribution in particular have remained obscure.

Interesting results have been obtained from investigation of the copolymerisation of hexachlorocyclotriphosphazen with other chlorocyclophosphazens. Although a patent report[33] that the rate and the yield of soluble polydichlorophosphazen in the polymerisation of this trimer are increased by the presence of 5–25% of octachlorocyclotetraphosphazen has not been confirmed[34], and additions of other higher chlorocyclophosphazens only slightly raise the yield of soluble product[35], study of the thermal copolymerisation of the trimer with its higher cyclic homologues has revealed the phenomenon of ring rearrangement, mostly involving increases in the proportion of tetramer and other homologues in the initial stages of polymerisation[36,37] (Table 1). This was first detected by Allen et al.[75], who synthesised polydichlorophosphazen by the thermal polymerisation (at 250 °C) of the trimer containing 2.9% of the tetramer, and found that increasing the duration of the process from 20 to 62 h not only raised the yield but also increased the content of higher homologues—especially pentamers and hexamers—in the mixture that had not reacted. However, at the time due attention was not paid to this interesting observation.

Table 1. Variation in composition of mixture of cyclic chlorophosphazens $(PNCl_2)_n$ during thermal block polymerisation at 250 °C[37]*.

3:4:5:6:7	W,%	ΔG, %			
		n=4	n=5	n=6	n=7
77 : 23 : 0 : 0 : 0	8	330	—	—	—
95 : 0 : 0 : 5 : 0	26	—	—	300	—
95 : 0 : 1 : 0 : 4	20	—	—	—	240**
95 : 0 : 1 : 0.1 : 3.9	14	—	126	730	260
90 : 0 : 2 : 1 : 7	8	—	92	300	120
85.5 : 9.5 : 1 : 0.25 : 3.75	24		106	450	210

*Column headings: 3:4:5:6:7 = proportions by weight in initial mixture of homologues having n = 3–7; W = yield of polydichlorophosphazen; ΔG = change in content of chlorocyclophosphazens (% on initial quantity of each ring).
**Total quantity of pentamer and heptamer.

Interconversions of rings have in general been known in phosphazen chemistry for a comparatively long time. Thus as early as 1960 Korshak et al.[38] observed the conversion of octaphenylcyclotetraphosphazen at 320–500 °C into a mixture of tri-, tetra-, penta-, and hexa-mers; hexakisheptafluorobutoxycyclotriphosphazen when boiled at 340 °C for 50 h is 50% converted into a tetramer[39]; and the reverse conversion of a tetrameric into a trimeric ring takes place when octachlorocyclotetraphosphazen is phenylated with phenylmagnesium bromide[40]. Interconversions of mixtures of cyclic chlorophosphazen homologues from trimer to heptamer during their vacuum distillation and in certain low-temperature (20–80 °C) nucleophilic substitutions have been reported recently[41], and also those of trimeric into tetrameric dimethylcyclophosphazens over the range 200–350 °C.[42] However, a distinguishing feature of this work[38-42] is that interconversions of chlorocyclophosphazens at 20–500 °C are not accompanied by polymer formation (except in the vacuum distillation of mixtures[41]).

In addition to the above work[36,37] formation of higher cyclic homologues from trimeric phosphazens has been observed by Allcock et al.[43] in a study of the thermal polymerisation of trifluoroethoxychlorocyclotriphosphazens $P_3N_3Cl_n(OCH_2CF_3)_{6-n}$ and the copolymerisation of hexachlorocyclotriphosphazen with the hexakistrifluoroethoxycyclotriphosphazen (I) (Table 2). Among the most important aspects of this work[43] pure (I) does not polymerise below 300 °C, but when heated at 275 °C for > 46 h, small quantities of the corresponding

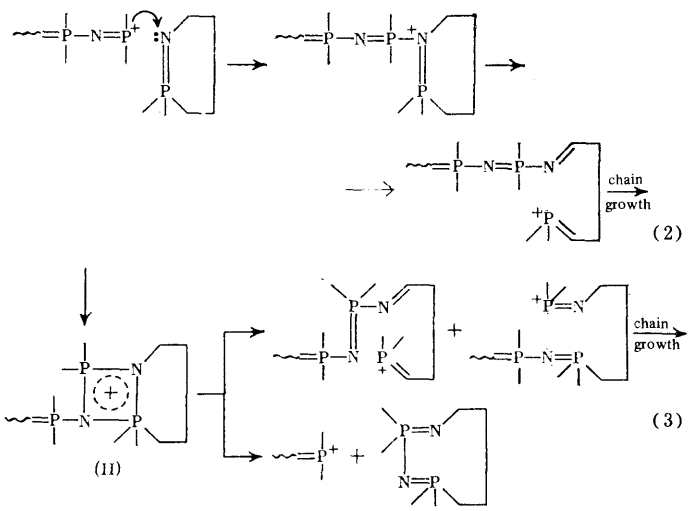
tetramer and pentamer are formed; copolymerisation of hexachlorocyclotriphosphazen and (I) takes place at 200 °C, at which temperature neither of the pure individual compounds polymerises; among partly substituted trifluoroethoxychlorocyclotriphosphazens only those having $n = 5-3$ undergo polymerisation; above 230 °C polycondensation takes place with the evolution of 2-chloro-1,1,1-trifluoroethane; and the molecular masses of the products of the above copolymerisation are lower than those resulting from the polymerisation of pure hexachlorocyclotriphosphazen.

Table 2. Copolymerisation of equimolecular quantities of hexakistrifluoroethoxycyclotriphosphazen (I) and hexachlorocyclotriphosphazen (III) at 200 °C[43]*.

t, h	(III):(I)	(I + III):(IV)	$PNCl_2$:$PN(OCH_2CF_3)_2$	t, h	(III):(I)	(I + III):(IV)	$PNCl_2$:$PN(OCH_2CF_3)_2$
24	1:1.3	1:0.024	—	32	1:2.0	1:0.:55	1:0.9
27	1:1.5	1:0.025	1:1.3	36	1:2 1	1:0.130	1:0.9
30	1:1.7	1:0.041	1:0.8	50	1:2.4	1:0.160	1:1.0

* Here t = duration of process; (I) and (III) given in mole proportions; (IV) = proportion by weight of (I + III) and other cyclic oligomers; and $PNCl_2 : PN(OCH_2CF_3)_2$ = mole proportions of $PNCl_2$ and $PN(OCH_2CF_3)_2$ units in copolymer.

The considerable increase in the content of higher chlorocyclophosphazens accompanying formation of polydichlorophosphazens in the initial stage of their copolymerisation with hexachlorocyclotriphosphazen has been explained[37] by specific interaction of the growing macrocation with cyclophosphazen molecules. The usual interaction (2) leading to further chain growth may be accompanied by an anomalous reaction involving formation of a cyclic transition state (II):



Localisation of the positive charge on either phosphorus atom of the four-membered ring (II) will entail its cleavage with increase in the length of the macrocation by the number of units of the initial ring. In view of the great stability of four-membered cyclic systems in phosphazen chemistry[44], however, it may be postulated that the transition state (II) can also break down at an exocyclic phosphorus–nitrogen bond (3). The additional structural units expanding the chlorophosphazen rings are thus provided by growing macrocations, which as a consequence of specific interaction with cyclic molecules (3) become one unit shorter, and this unit is incorporated into the ring under attack, which becomes larger.

Reaction (3) can evidently take place also with $-N=P<$ units of linear macromolecules that have already been formed, and the proportion of such interaction will increase with the degree of conversion. It may provide one reason for the observed wide molecular-mass distribution of polydichlorophosphazen. Determination of the proportions of reactions (2) and (3) in an actual process must obviously take into account both structural and thermodynamic factors. The strain in a ring, which governs the energy of its vapour-phase polymerisation, may differ substantially for different conformers[45]. For example, the difference in strain between crenulated planar and buckled C_2 forms of the cyclic pentamer, which characterise crystalline and liquid states respectively, is 18.75 kJ mole^{-1}.

Table 3. Polymerisation of fluoroalkoxychlorocyclotriphosphazens[46].

Cyclophosphazen	R_FO:Cl	T, °C	t, h	W *, %	$[\eta]$, dl g^{-1}
$(C_2F_5CH_2O)_2P_3N_3Cl_4$ (V)	0.5:1	200	80	70.5	0.55
$(C_3F_7CH_2O)_2P_3N_3Cl_4$	0.5:1	200	120	73.0	0.50
(V) + $(C_2F_5CH_2O)_6P_3N_3$ **	1.24:1	260	90	76.2	***
$(C_2F_5CH_2O)P_3N_3Cl$	5:1	270	100	0	
$(C_2F_5CH_2O)_nP_3N_3Cl_{6-n}$ ****	2.23:1	270	100	0	

* Yield of polymer.
** Mixture of 53% (V) + 47% $(C_2F_5CH_2O)_6P_3N_3$.
*** Polymer swells strongly but does not dissolve.
**** Contents of homologues having $n = 3-6$ respectively 25%, 50%, 10%, and 15%.

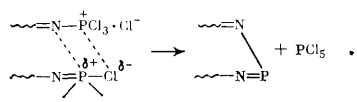
The presence of ring substituents other than chlorine atoms will also influence the probability of formation of transition state (II), so that the capacity of partly substituted chlorocyclophosphazens for thermal polymerisation becomes significant. Even before the appearance of Allcock's work[43] it had been reported[46,47] that fluoroalkoxychlorocyclotriphosphazens can polymerise at 200 °C. The process occurred only when $R_FO : Cl \leq 2 : 1$ (Table 3). When mixtures of hexachlorocyclotriphosphazen with hexakisperfluoroalkoxycyclotriphosphazen or other mixtures satisfying the above ratio are used, polymerisation is apparently preceded by exchange of substituents[48], which is not excluded by Allcock et al.[43]

In the polymerisation of fluoroalkoxychlorocyclotriphosphazens, however, the proportion of polycondensation processes accompanied by separation of a fluoroalkyl chloride increases with rise in temperature[43]. Such processes take place at lower temperatures with non-fluorinated alkoxyphosphazens—e.g. at 150–170 °C with butoxychlorocyclotriphosphazens[49]—although polycondensation of the latter with separation of butyl chloride and formation of polymers containing P–O–P links between phosphazen rings is also accompanied[50] by polymerisation with ring opening.

It is therefore more interesting, from the point of view of capacity for polymerisation, to investigate alkylchlorocyclotriphosphazens containing the more stable phosphorus–carbon bonds. Trimethyltrichlorocyclotriphosphazen, tetramethyltetrachlorocyclotetraphosphazen, and their mixtures are polymerised[51] at 200–220 °C after 15–20 h, with formation of a rubberlike product having viscosity $[\eta] = 0.5–0.7$ dl g^{-1}. Use in the thermal polymerisation of hexachlorocyclotriphosphazen of additions of its partly substituted derivatives of general formula $R_xP_3N_3Cl_{6-x}$ (R = CH_3, CF_3CH_2O, or other fluoroalkoxyl; $x \leq 1.5$) not only shortens the process but also raises the yield of soluble polydichlorophosphazen[52].

In an investigation of the thermal polymerisation of a series of phenylhalogenocyclotriphosphazens Allcock and Moore established[53] that only the phenylpentafluoro-compound is capable of homopolymerisation at 300 °C: geminal and non-geminal compounds $(C_6H_5)_nP_3N_3Cl_{6-n}$ having $n = 2–6$ do not polymerise at this temperature, although at 250 °C homologues in which $n = 2$, 3 copolymerise with an equimolecular proportion of hexachlorocyclotriphosphazen, but products in which $n = 4–6$ inhibit polymerisation of the latter. The copolymers have a considerably lower molecular mass than has the polydichlorophosphazen obtained by its homopolymerisation. Results[47,53] are fully consistent with the above mechanism of chain growth (schemes 2 and 3). Attempts to effect the catalytic polymerisation of hexaphenyl- and hexaphenoxy-cyclotriphosphazens in the presence of strong acids gave only a low yield of oligomeric products, whose formation involves intermediate detachment of side-groups[54–56]. Yet a report appeared on the thermal polymerisation of an aryloxypentachlorocyclotriphosphazen[57], essentially by a modification of the method of Ref.12.

Among other methods for obtaining polydichlorophosphazen is its synthesis from linear oligomers $Cl_3P{:}N.[PCl_2{:}N]_n.PCl_4$ ($n = 3–15$) by prolonged heating at 240–260 °C. The process is accompanied by separation of phosphorus pentachloride, obviously by the reaction of terminal groups[58]:



Thermal degradation of polydichlorophosphazen is a first-order reaction having activation energy 92.11 kJ mole^{-1} and yielding a large number of oligomeric linear and cyclic homologues[59]. It is assumed to involve ionic terminal groups, which is consistent with the known[1,2] equilibrium character of the polymerisation of chlorocyclophosphazens.

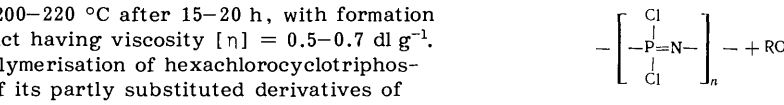
X-Ray examination of polydifluorophosphazen–the phosphazen polymer having the smallest of known side-groups–has yielded interesting results[60]. This polyphosphazen can be present as two conformers: conformer A exists between −36 and +25 °C, and has a repeat distance of 6.49 Å; conformer B is observed at around −56 °C, and has repeat distance 4.86 Å (for polydichlorophosphazen 4.96 Å). The latter conformer has a *cis–trans* planar chain conformation with P–N–P and P–F bond lengths 1.52 and 1.47 Å, and PNP, NPN, and FPF angles 136°, 119°, and 95° respectively. The density of polydifluorophosphazen at 25 °C is 1.84 g cm^{-3}.[60]

III. POLYORGANOPHOSPHAZENS

Interest in the synthesis of macromolecular linear polyphosphazens has grown considerably during recent years[61–63] in connection with the problem of producing thermostable and non-flammable rubbers having good resistance to cold.

1. Polydialkoxyphosphazens

These polyphosphazens are obtained by replacing chlorine atoms in polydichlorophosphazen by alcohol or phenol residues:



where R = Alk, Ar and M = alkali metal. The main trends in research during recent years have been the synthesis of polyperfluoroalkoxyphosphazens as potential fire-resistant and thermostable rubbers having high chemical stability and resistance to cold, investigation of the effect of the nature of side-groups on the chemical and physicochemical properties of such polymers, study of the possibilities of using polydialkoxyphosphazens for biomedical purposes, and a search for methods of vulcanisation and stabilisation.

It had been shown earlier[1] that polyphosphazens having identical lower perfluoroalkoxy-groups in the side-chain are in most cases crystalline. In order to obtain elastomeric products, therefore, the synthesis of polymers containing various groups–perfluoroalkyl[65–70] or mixed alkoxy-substituents[71,73,79–83]–has been investigated.

Table 4. Some properties of polyphosphazen copolymers $-[N{:}P(OR)(OR')]_n-$*.

R	R'	R:R'	$10^{-5}M$ ([η], dl g^{-1})	T_{gl}, °C	T_{decomp}, °C**	Ref.
CF_3CH_2	$C_3F_7CH_2$	1:1	50(1.46)	−71(−77)	300	[67]
CF_3CH_2	C_6H_5	1:1	(3.50)	—	460	[65]
CF_3CH_2	C_6H_5	1:1	(1.14)	−35	—	[105]
CF_3CH_2	$HC_6F_{12}CH_2$	1:1	(1.50)	−64	—	[67,69]
CF_3CH_2	$HC_4F_8CH_2$	1:1	—	−67	—	[67,69]
CF_3CH_2	$HC_4F_8CH_2$	1.9:1	(1.20)	−68	—	[92]
CF_3CH_2	$C_6H_4C_6H_4O$-*p*	1:0	—	−70	260	[70]
CF_3CH_2	$C_6H_4C_6H_4O$-*p*	0.4:1.6	—	−10	355	[70]
CF_3CH_2	$C_6H_4C_6H_4O$-*p*	0:1	—	43	320	[70]
$H(CF_2)_2CH_2$	C_6H_5	1:1	(1.32)	−50	—	[105]
CF_3CH_2	C_6H_4Cl-*p*	1:3	(1.03)	−20	—	[105]
CF_3CH_2	C_6H_4Cl-*p*	1:1	(0.84)	−25	—	[105]
$H(CF_2)_2CH_2$	C_6H_4Cl-*p*	1:1	(0.92)	−40	—	[105]

* Macromolecules may contain doubly and singly substituted phosphorus atoms.

** T_{decomp} = temperature at which decomposition begins.

Polyperfluoroalkoxyphosphazen copolymers are most often obtained from mixtures of trifluoroethoxides with fluorinated higher alkoxides[65–69] and also with phenoxides[65,81,105]. Sodium alkoxides are usually employed, although in some cases the lithium compounds are more effective[74]. Substitutions are conducted predominantly in oxolan, dioxan, diglyme, and their mixtures with benzene; the last is usually employed to dissolve polydichlorophosphazen. In order to increase the conversion the concluding stages are carried out at high temperatures, especially when aryloxy-groups are introduced[70,75–77]. Almost complete replacement of chlorine can thus be achieved, although this is influenced by various uncontrollable factors, assumed[78] to be connected mainly with the stage of polymerisation of hexachlorocyclotriphosphazen in the synthesis of polydichlorophosphazen.

By varying the nature and the proportions of side-groups it is possible to change within wide limits such properties of polydialkoxyphosphazens as solubility, glass temperature,

molecular mass and molecular-mass distribution, thermal stability, processability by various methods, etc.[78-85,89,91,92]. For this purpose substitution is effected with mixtures of alcohols and phenols[65,70,81,89], fluorinated C_{4-12} alcohols[79], and mixtures of phenols[80,83]. The properties of homoaryloxyphosphazens can be controlled by varying the nature and the position of constituents in the initial phenol[76,77,82]. Table 4 lists some of the properties of polyalkoxyphosphazen copolymers, among the most interesting of which are those of trifluoroethoxy- and octafluoropentyloxy-phosphazens. Thus a copolymer containing 65 mole % of CF_3CH_2O groups and 35 mole % of $H[CF_2]_4CH_2O$ groups has a glass point of −68 °C and does not swell in hydrocarbons; 86% of this copolymer comprises a macromolecular fraction having $\bar{M}_n$ = 1370600 and $\bar{M}_{wt}$ = 4085800 (M_{wt}/M_n = 3), whereas corresponding values for the unfractionated copolymer are 123700 and 3514500 (28.4).[92] The high polydispersity is evidently due to the presence of a considerable proportion of fractions of low molecular weight. For this copolymer the viscosity $[\eta] = 0.00488\bar{7}M_n$.[1,47]

Even with equimolecular proportions of the initial substituting reagents the resulting copolymers contain three types of units—two paired, NPR_2 and NPR'_2, and the mixed NPRR′—in quantities determined by (apart from the proportions of the initial reactants) the dimensions and the inductive properties of the new substituents. The presence in various combinations of three types of monomer units in the macromolecules of polyalkoxyphosphazen copolymers is responsible for their hyperelastic properties over a wide temperature range.

The low glass point of polyfluoroalkoxyphosphazens is due to the high thermodynamic flexibility of the main chain and the absence of side-group interactions. Introduction of bulky aromatic groups in the place of chlorine, however, raises the glass point, which is especially clearly shown[70] by the polyphosphazen copolymers $-[N{:}P(OCH_2CF_3)_{2-x}.(OC_6H_4C_6H_5\text{-}p)_x]-$. These copolymers are obtained by treating a solution of polydichlorophosphazen in benzene successively with a phenoxide and an alkoxide in oxolan, and are purified by reprecipitation from oxolan solution into water. In oxolan at 25 °C the copolymers have viscosities in the range $[\eta]$ = 1.06–2.20 dl g^{-1}, which fall with decrease in x; their molecular mass $\bar{M}_n = (0.9–3.3) \times 10^5$ (measured osmometrically in cyclohexanone). Fractionation showed the copolymers to be inhomogeneous with respect to composition: thus for a product having x = 0.15 this parameter is 0.32 for the fraction of high molecular weight, and 0.08 for that of low molecular weight. Heating the copolymers in air at 150 °C for 12 h lowers their viscosity $[\eta]$ by factors of 4–5. X-Ray examination shows the copolymers to be relatively disordered, with crystallites formed by the crystallisation of microblocks comprising $-N{:}P(OCH_2CF_3)_2-$ units, the presence of which is confirmed by the fluorine-19 nuclear magnetic resonance spectra[70].

A convenient method for the synthesis of polydialkoxyphosphazen copolymers is the transetherification of alkoxylated polymers with higher alcohols; alkoxides of the latter are used to obtain polyperfluoroalkoxyphosphazens[73,85]. Besides the alkoxide–phenoxide method an acceptor method is also available for the synthesis of polyalkoxyphosphazens[86,90,106,107]. Thus, when trifluoroethanol in oxolan at 60 °C is used to replace chlorine atoms in polydichlorophosphazen, the degree of substitution reaches 65% after 5 h, and a limiting value of 85% after 100 h; introduction of lithium chloride into the reaction mixture increases this to 90%. However, substitution is accompanied by side-reactions of polydichlorophosphazen with triethylamine and other processes, so that the heterounit character of the resulting polymer reaches 6.8%.[86] Nevertheless, the acceptor method of substitution in polydichlorophosphazen is more convenient for preparative purposes[50,106,107].

Several polyaryloxyphosphazens having identical side-groups have been synthesised and characterised[75-77]. These polymers are soluble in dimethylformamide and oxolan, have viscosities $[\eta]$ = 0.8–12 dl g^{-1} (Table 5), and are shown by X-ray examination to be only slightly ordered with glass points between −40 and +50 °C. Polydialkoxyphosphazens $\{[P(OR)_2{:}N]_2.P(OR)(OR'){:}N-\}_n$ with regularly alternating (every two phosphorus atoms) R′ groups are obtained by the action of alkoxides or phenoxides on linear polymerisation products of monoaryloxypentachlorocyclotriphosphazens $R'OP_3N_3Cl_5$.[12,133]

Table 5. Polydiaryloxyphosphazens $-[PN(OAr)_2]_n-$.

Ar	$[\eta]$, dl g^{-1}*		T_{gl}, °C	M.p., °C	T_l, °C***	Ref.
	initial polymer	after heating**				
C_6H_5	2.4	—	−1	160	400	[77]
m-ClC_6H_4	1.5	0.08	−35	—	380	[76]
p-ClC_6H_4	1.4	0.42	−12	—	400	[76]
p-ClC_6H_4	1.6	—	5	167	385	[77]
2,4-$Cl_2C_6H_3$	12.0	1.5	2	—	440	[76]
p-FC_6H_4	9.0	—	−14	—	385	[76]
p-$CH_3C_6H_4$	1.8	—	3	152	310	[77]
m-$CH_3C_6H_4$	1.8	—	−25	90	340	[77]
p-$C_2H_5C_6H_4$	3.2	—	−36	43	250	[77]
o-$CH_3OC_6H_4$	1.8****	—	6	125	330	[77]
β-$C_{10}H_7$	1.9*****	0.5	47	—	475	[76]
p-$C_6H_4C_6H_4$	1.2*****	0.7	43	—	390	[76]

* Measured in oxolan at 25 °C.
** At 255 °C for 8 h.
*** T_l = temperature of 10% loss in mass.
**** In chloroform.
***** In dimethylformamide.

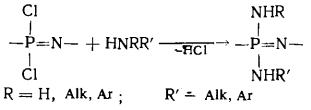
Table 6. Polybisarylaminophosphazens $-[PN(NHAr)_2]_n-$.

Ar	$[\eta]$ *dl g^{-1}*	T_{gl}, °C	T_{decomp}, °C**	Ref.
C_6H_5	1.4	105	—	[87]
C_6H_5	1.2	98	—	[88]
p-$CH_3C_6H_4$	1.3	97	250	[87]
p-$CH_3C_6H_4$	1.1	95	—	[88]
p-$CH_3OC_6H_4$	1.3	92	266	[87]
p-$CH_3OC_6H_4$	1.2	90	—	[88]
p-$C_2H_5C_6H_4$	0.7	61	243	[87]
m-$C_2H_5C_6H_5$	1.5	53	253	[87]
n-$C_4H_5C_6H_4$-p	0.9	92	266	[87]
p-ClC_6H_4	0.6***	85	265	[87]
p-ClC_6H_4	1.0***	70	—	[88]
p-ClC_6H_4	1.3***	80	253	[87]
p-FC_6H_4	0.7***	—	260	[87]
m-FC_6H_4	0.3***	80	249	[87]

* Measured in oxolan at 25 °C.
** From dynamic thermogravimetric analysis in air, ΔT = 20 deg min^{-1}.
*** In chloroform.

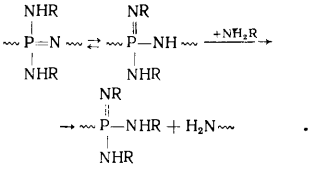
2. Polydiaminophosphazens

Polydiaminophosphazens are obtained by replacing chlorine atoms in polydichlorophosphazen with residues of primary or secondary amines:



Either the initial amine or a specially added tertiary amine can act as acceptor of the hydrogen chloride formed[87,88,94-96].

Polybisarylaminophosphazens have higher glass points (Table 6) than have polydiaryloxyphosphazens, as a consequence of the greater rigidity of chains due to hydrogen bonding in the former[87,88]; a similar pattern is observed on comparing corresponding polydialkoxyphosphazens[1,9] and polybisalkylaminophosphazens[94-96]. The latter differ from the former in possessing an ordered structure (Table 7), although their formation is accompanied by degradative processes, as is indicated by the considerably lower molecular mass in comparison with the initial polydichlorophosphazen or corresponding polydialkoxyphosphazens[96]. This may be due to the reaction [87]



When primary amines are used as substituting reagents, however, the molecular mass may be increased by partial cross-linking[96]

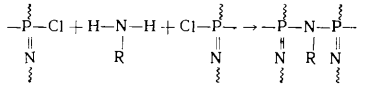


Table 7. Polybisalkylaminophosphazens $-[N{:}P(NHR)(NHR')]-$[96].

R	R'	M.p., °C	T_{gl}, °C	M_z***	[η], dl g^{-1} (solvent, t °C)
$NHCH_3$	$NHCH_3$	140	14	8.1	2.0 (water, 30°)
NHC_3H_7	NHC_3H_7	151	4	—	1.1 (trifluoroethanol, 30°)
NHC_4H_9	NHC_4H_9	139	8	—	2.5 (trifluoroethanol, 30°)
$NHCH_3$	$N(C_2H_5)_2$	174	8	23.0	1.4 (benzene, 30°)
NHC_2H_5	$N(C_2H_5)_2$	111	−11	27.4*	1.2 (benzene, 30°)
NHC_3H_7	$N(C_2H_5)_2$	—	−5	13.2**	1.2 (benzene, 30°)
NHC_4H_9	$N(C_2H_5)_2$	—	−6	15.5	1.4 (benzene, 30°)

* $\bar{M}_n = 1.55 \times 10^5$.
** $\bar{M}_n = 1.27 \times 10^5$.
[***M_z = molecular weight by ultracentrifugation (Ed. of Translation)].

Polyaminophosphazens are chemically stable. The use of alkyl esters of amino-acids[97,98], however, entails not only increase in the proportion of degradative processes in main chains and decrease in degree of substitution with bulky ligands but also diminished chemical stability of the polyphosphazens, which begin to decompose even at room temperature.

When sterically hindered nucleophiles, e.g. *p*-phenylazoaniline[99], derivatives of other colorants or steroids[100], are used for the preparation of polyphosphazens, at most one chlorine atom can be substituted at each phosphorus atom in polydichlorophosphazen, and the activity of the remaining chlorine atoms is sharply diminished even towards such highly active reagents as sodium trifluoroethoxide and methylamine[100].

An original method for synthesising polybistrifluoroethoxyphosphazen[101] consists in heating tristrifluoroethoxy-*N*-trimethylsilylphosphazen at 200 °C. Trifluoroethoxytrimethylsilane separates and a polymer of molecular mass 4000–10000 is formed.

3. Polyalkylphosphazens

Since alkylated cyclophosphazens cannot be polymerised, polyphosphazens containing organic groups attached by a carbon–phosphorus bond are obtained by the action of various organometallic compounds on polyhalogenophosphazens. Thus boiling polydichlorophosphazen in benzene with a double excess of phenyl-lithium gives a 22% yield of polydiphenylphosphazen[102]. Polydifluorophosphazen reacts more readily with phenyl-lithium, and also with diethyl- and dibutyl-magnesium[103], although in this case, too, only one halogen atom on each phosphorus atom is replaced preferentially. Thus an attempt to replace all the fluorine atoms in polydifluorophosphazen enabled only 80–90% substitution to be attained, with considerable degradation of macromolecules[103,104].

Table 8. Molecular-mass and physicochemical characteristics of polyphosphazens $-[PNR_2]_n-$.

R	$10^{-3}\bar{M}_n$	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$10^4 A_2$*, cal mole g^{-2}*		$\langle S^2\rangle^{1/2}_z$**, Å	ΔC_p, cal g^{-1} deg^{-1}	ρ_{25}, g cm^{-4}	Ref.
				osmometry	light scattering				
C_6H_5NH	0.87	11.6	13.4	−0.055	−0.072	548	0.048	1.289	[88]
p-$CH_3C_6H_4NH$	0.93	15.3	16.5	+0.007	+0.007	665	0.050	1.172	[88]
p-$OCH_3C_6H_4NH$	1.24	18.2	14.7	0	0	418	0.064	1.240	[88]
p-ClC_6H_4NH	0.55	7.6	13.9	−0.015	−0.033	479	0.032	1.440	[88]
C_6H_5O	1.3	6.1	4.7	+1.440	—	348	—	—	[77]
p-ClC_6H_5O	2.2	21.3	9.7	+1.600	—	638	—	—	[77]

* Second virial coefficient.
** Hydrodynamic radius.

IV. PROPERTIES OF POLYPHOSPHAZENS

Molecular-mass Characteristics

These characteristics of polyphosphazens have been the subject of lively discussion, primarily because of the unusually wide molecular-mass distribution noted by many workers[1,76-78,87,88,95,96]. Thus the polydispersity coefficient of polyaryloxyphosphazens may reach 30,[76] and amounts to 5–10 even for individual fractions; in most cases gas-absorption chromatography indicates a bimodal distribution for these polymers[70,78], the origin of which is still obscure. Nor has the reason been ascertained why radii of inertia of

macromolecules found from light scattering considerably exceed the calculated values: $\langle S^2\rangle^{\frac{1}{2}} = 546$ or 638 nm[76,77] for polydi-p-chlorophenoxyphosphazen, but 600–1300 nm[78] for the corresponding *m*-chlorophenoxy-derivative. The calculated value for phosphazen chains having $M = 10^6$ is $\langle S^2\rangle^{\frac{1}{2}} = 40$–50 nm. Such a substantial divergence is assumed[76,78] to be due to a wide molecular-mass distribution or a branched character of the macromolecules.

Similar anomalies are observed with polybisarylaminophosphazens (Table 8). The identical character of molecular-mass characteristics for polyphosphazens having different types of side-groups indicates that the distributions are "prescribed" during formation of the initial polydichlorophosphazen. This hypothesis is confirmed by results[114] showing a significant difference between the molecular-mass distributions of polyphosphazens prepared from polydichlorophosphazen and those obtained by the polymerisation of hexachlorocyclotriphosphazen in the mass and in solution.

Structure of Polyphosphazens

Little work has yet been done on structure, although definite progress has been noted in recent years. Thus two transition points have been observed[8,108–112] in certain partly crystalline polyphosphazens, the difference between which may reach 150–250 deg. The first T_1 corresponds to a transition from an ordered three-dimensional to a mesomorphous state. In polybischlorophenoxyphosphazens the latter is characterised by a pseudohexagonal structure with two-dimensional order in the packing of parallel oriented chains[108]. Study of polybistrifluoroethoxyphosphazen by optical microscopy, nuclear magnetic resonance, X-ray diffraction, and differential scanning calorimetry[109,110] has revealed spherulitic morphology remaining unchanged on passage through the first transition point, although this is accompanied by disruption of ordered orientation of macromolecular axes and a transition to structures with hexagonal packing. These transition temperatures and melting points are given for several polyphosphazens in Table 9.

Table 9. Transition and decomposition temperatures of polyphosphazens $-[PN(OR)_2]-$[8].

R	T_{gl}, °C	Transition temp., °C		T_{decomp}, °C**
		T_1^*	m.p.	
CF_3CH_2	−66	90	240	360
C_6H_5	6	160	390	380
m-ClC_6H_4	−24	66	370	380
p-ClC_6H_4	4	167	365	410
C_6H_5 + *p*-ClC_6H_4 (1 : 1)	5	77, 94	—	—

* T_1 = temperature of transition to liquid-crystalline state.
** From dynamic thermogravimetric analysis in air.

The mesomorphous transitions in polyphosphazens are characterised by considerable enthalpy changes, exceeding those for a transition into the isotropic melt by factors of 10 and > 50 in polybistrifluoroethoxyphosphazen and polydi-*p*-chlorophenoxyphosphazen respectively[109] (Table 10). This feature is more characteristic of liquid-crystalline systems of low molecular weight[113]. The discrepancies in transition points and melting points given by different workers (Tables 9 and 10) are apparently due to the dependence of these temperatures on the preliminary annealing conditions. Thus the former polymer exhibits a significant dependence of the transition point on the conditions of crystallisation, the temperature, and the duration of the anneal (Fig.1).[109] The highest value (T_1 = 91.5 °C) and the maximum heat of transition are achieved after the polymer has been preheated in the range 240–255 °C.[109]

Table 10. Transitions in polyphosphazens and other compounds[109]*.

Compound	T_1, °C	M.p., °C	ΔH, cal g^{-1}, at		$\Delta V(T_1)$	ΔV(m.p.)
			T_1	m.p.		
Polybistrifluoroethoxyphosphazen	92	240	8.6	0 8	5	6
Polydi-*p*-chlorophenoxyphosphazen	169	356	6.6	0	3.5	5.7
Polyethylene	—	141	—	68	—	15
p-Azoxyanisole	116	133	28.0	0 7	0.10	0.36

* ΔH = change in enthalpy; ΔV = volume change, %.

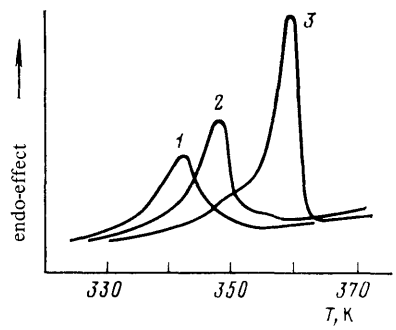


Figure 1. Effect of heat-treatment on the endotherms for the transition of polybistrifluoroethoxyphosphazen from the crystalline to the mesomorphous state: 1) specimen obtained from melt by moulding (T_1 = 79.5 °C); 2) as (1) after recrystallisation by cooling from 112 °C at 20 deg min^{-1} (80.5 °C); 3) specimen preheated at 240–255 °C (91.5 °C).

Dynamic mechanical tests on polybistrifluoroethoxyphosphazen have shown[76,112] a sharp decrease in modulus of elasticity at the transition point, at or slightly above which the polymer can already be moulded under pressure into strong flexible films. Despite considerable interest in the mesomorphous state of polyphosphazens, it is not yet clear what type of structure it possesses—whether smectic, nematic, or plastic crystalline.

Amorphous polyphosphazens can be assumed to have a globular structure in view of the great flexibility of the macromolecules[1] and by analogy with amorphous polysiloxanes. This hypothesis is consistent with the closely similar permeabilities of these two groups of polymers to water vapour and diffusion coefficients of the vapour in them[114, 115]. Mixtures of partly crystalline homopolymers differ from the corresponding phosphazen copolymers in having a single glass point and several transition points T_1, which indicates

compatibility of the amorphous phases and absence of such compatibility from crystalline regions[116].

Like polydichlorophosphazen[28] its isothiocyanato- and alkylamino-derivatives[117,118], in contrast to corresponding cyclic analogues, exhibit predominantly electronic conduction.

Chemical Properties

The chemical properties of polyphosphazens are determined in considerable measure by the nature of the side-groups. The completely substituted compounds containing inert aliphatic and aromatic groups attached to phosphorus atoms of the main chain directly through oxygen or nitrogen atoms resist the action of atmospheric moisture and weak acids and bases[1,8]. Thus polydiphenylphosphazen remains unchanged after being boiled in 1 *N* nitric acid and 1 *N* aqueous potassium hydroxide for 48 h.[102] Polymers containing residues of amino-acids in the side-chain, however, readily undergo spontaneous decomposition when stored under normal conditions[97].

Thermal Stability

Polyphosphazens containing organic substituents are considerably less stable than the original polydichlorophosphazen, which begins to depolymerise only above 350 °C,[1,8] a first-order reaction having activation energy 98 ± 8 kJ mole^{-1}.[119,126] The temperatures given in Tables 5, 6, and 9 for the start of decomposition of various polyphosphazens were obtained by dynamic thermogravimetric analysis. However, viscosimetric measurements indicate that macromolecules of most of the organically substituted polyphosphazens begin to break down over the range 100–200 °C.[78,119–121]

Polybisalkylaminophosphazens are thermally the most stable, like their cyclic analogues beginning to undergo deaminolysis above 100–150 °C.[1,8,122] Polydialkoxyphosphazens are somewhat more stable, although both polydiphenoxy- and polydi-*m*-chlorophenoxy-phosphazens[119,78] exhibit a decrease in molecular mass over the range 130–160 °C. In contrast to the results of dynamic thermogravimetric analysis (Table 9), polybistrifluoroethoxyphosphazen is relatively thermostable under conditions of isothermal heating and resembles most other polyperfluoroalkoxyphosphazens in decomposing under equilibrium and non-equilibrium conditions with the formation of cyclic homologues[120,121].

Experimental results at present available indicate that the thermal stability of polyphosphazens is determined by the factors—thermal stability of side-groups, presence of weak, defective chain units resulting from incomplete substitution and other causes, steric interactions of side-substituents facilitating breakdown of the main chain, and degradation governed by the influence of terminal groups.

The influence of the nature of side-groups on the thermal stability of polyphosphazens is illustrated by polybisalkylaminophosphazens (Table 6)[37,88,122]. The presence of defective units is apparently responsible for cases of regular increase in molecular mass of polydiaryloxyphosphazens at 130–170 °C.[78,119] This is indicated by the formation of a small quantity of 2-chloro-1,1,1-trifluoroethane in the degradation of polybistrifluoroethoxyphosphazen[120]. Instability due to steric interactions of bulky side-groups has been examined in detail by Allcock[1,127,128].

With small and thermally stable side-groups (e.g. trifluoroethoxy) and with a sufficiently high degree of substitution, however, terminal groups begin to play an important part in the thermal stability of polyphosphazens. Thus it was shown[123] for polydibutoxyphosphazens that, as the molecular mass decreases and the concentration of terminal P:O and P.OH groups increases, the rate of degradation in a vacuum (0.133 Pa) at 200 °C rises, while the character of the weight-loss curves changes owing to depolymerisation with formation of cyclic butoxyphosphazens (Fig. 2). At higher temperatures (220–250 °C) the molecular mass of the polymer has hardly any effect on the character of degradation: under these conditions instability of side-groups obviously becomes the dominant factor. As decomposition diminishes (residual pressure 266 Pa), dibutyl ether and tributyl phosphate appear among the volatile degradation products[123].

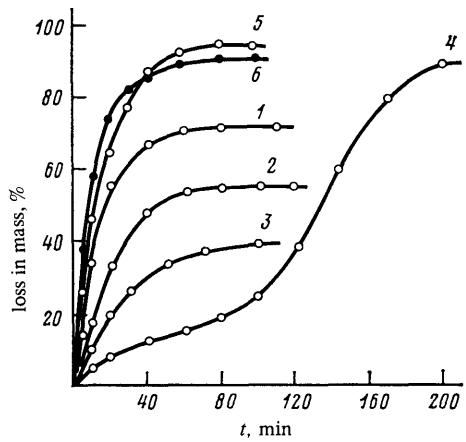
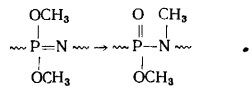


Figure 2. Thermal degradation of polydibutoxyphosphazens in a vacuum (0.133 Pa) at (°C) (molecular mass): 1) 200 (1340); 2) 200 (3100); 3) 200 (5400); 4) 200 (750000); 5) 220 (750000); 6) 250 (750000).

Establishment of the influence of the nature and concentration of terminal groups in polydialkoxyphosphazens on their thermal degradation has enabled coordinated polyphosphazens of chelate type to be obtained from analogous linear oligomers[124]. The thermal stability of polyphosphazens can be enhanced by the chemical blocking of terminal groups and also groups responsible for initiating the thermal breakdown of other weak bonds in macromolecules. Thus thiocarbonate derivatives of zinc and lead[129], oxides, hydroxides, and carbonates of alkali and alkaline-earth metals, quinolinol complexes of transition metals[130], a zinc derivative of mercaptobenzothiazole[131], and zinc hippurate[132] are used to stabilise polyphosphazens.

Among other thermal reactions of polyphosphazens mention must be made of the phosphazen–phosphazan rearrangement, which takes place in polydimethoxyphosphazen at 130 °C[125]:



After 6 h the degree of conversion into a polymeric phosphazan is 34.7%.

Vulcanisation of Polyphosphazens

Vulcanisation is acquiring increasing importance in view of the great practical value of these polymers. Traditionally, unsaturated groups are introduced into side-chains, and

vulcanisation is effected with peroxides[134,135]. In the case of polyaryloxyphosphazens, polymers containing unsaturated groups—mostly allyl[136,137] or alkenyl[90]—in the aryloxy-radicals are used. These polymers can be hardened also by heating with sulphur or by the action of ionising radiations[137,138,143].

In order to lower the temperature of the vulcanisation of polyphosphazens primary and secondary amino-groups[139] or hydroxyalkyl radicals[140] are introduced in their side-chains; such polymers can be cross-linked at moderate temperatures by the action of diazocyanates, polyanhydrides, and diepoxides. Polyphosphazens containing unsaturated bonds in side-chains can be vulcanised at room temperature by means of oligomeric siloxanes containing silicon–hydrogen bonds, the process being accomplished in the presence of catalysts containing platinum[141]. It has been suggested[73,142] that polyperfluoroalkoxyphosphazens could be cross-linked by treatment with alkoxides of perfluoroglycols.

V. APPLICATIONS

The main trends in the application of macromolecular polyphosphazens have been[6-10] the production of elastomers and hence articles able to withstand low temperatures and aggressive media, the preparation of non-flammable and incombustible materials, and biomedical uses. The most promising elastomers have been obtained from polyperfluoroalkoxyphosphazen copolymers, e.g. $\{(CF_3CH_2O)_x(H[CF_2]_4.CH_2O)_{2-x}PN\}$, and also polymers containing other perfluorinated alcohol residues[7,8,67,145].

Table 11. Fire resistance of polymers[7,148].

Polymer	O.i.	D_{sm}*
Polyethylene	17	150
Polystyrene	18	468
Polydimethylsiloxanes	26	385
Polycarbonates	27	660
Polyvinyl chloride	44	525
Polybistrifluoroethoxyphosphazen	67	—
Polydiaryloxyphosphazens $[PN(OC_6H_4R)_2]_x$		
R = H	33	343
R = *p*-Cl	44	455
R = *p*-Br	65	—
R = *p*-OCH_3	26	120
R = H, C_2H_5 (copolymer)	43**	40

* Obtained on testing in a smoke chamber.
** Copolymer filled with 50 mass % of aluminium hydroxide; the unfilled copolymer has O.i. = 28.

Elastomers are obtained by adding to the initial polyperfluoroalkoxyphosphazens 30–40 mass % of reinforcing fillers (carbon black, Aerosil, clay, aluminium hydroxide, etc.) and also vulcanising and stabilising agents. Those resulting from the vulcanisation of such mixtures have good low-temperature properties, modulus of elasticity at 100% elongation 3.5–10.5 MPa, tensile strength 7.0–14.0 MPa, and elongation at break 100–200%. They resist the action of oils, liquid fuels, and hydraulic fluids, and can operate at temperatures up to 175 °C for a long time[7,145]. Such elastomers are used to make flange seals, airtight and damping packing, glands, fuel hoses, and other components employed in aviation and other branches of technology[144,146,147].

Polyphosphazens have been widely used to obtain fire-resistant and non-flammable polymeric materials. Table 11 compares oxygen indices (O.i.) and specific optical densities of smoke D_{sm} for the combustion of several industrial polymers and polyphosphazens. The latter are either incombustible (O.i. > 30) or self-extinguishing (> 25). Polyphosphazens have the advantage over difficultly combustible or self-extinguishing organic polymers (polyvinyl chloride, polycarbonates) of forming less toxic products on combustion or thermal decomposition[149,150]. The presence of halogens in organic side-chains improves considerably the fire-resistance of polyphosphazens[7,148,149].

An interesting field of application of polydialkoxyphosphazen homopolymers and copolymers is the production of elastic and semi-rigid foams[149,151].

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The Dilatancy of Colloidal Structures and Polymer Solutions

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The dilatant regime in the flow of dispersions under the constrained conditions of the interaction of colloidal particles resistant to aggregation is discussed. In this case the system behaves as a dilatant periodic colloidal structure of the second type with a limited volume of the medium (PCS_2) in which a positive disjoining pressure $\pi_2 > 0$ operates. The similarity in the dilatant behaviour of dispersed systems and structured solutions of surfactants and polymers is demonstrated. With increased concentration of ions (and also of particle size), the dilatant regime passes into an anomalously viscous (thixotropic regime), i.e. under these conditions the dilatant PCS_2 is converted into a thixotropic PCS_1 (of the first type) in which $\pi_1 < 0$.
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I. INTRODUCTION

The unusual rheological properties of colloidal structures, which usually exhibit a non-Newtonian viscosity, have already been investigated for a long time. However, until recently most interest was shown in the behaviour of dispersions, whose shear deformation is accompanied by an appreciable decrease of the effective viscosity as a consequence of the breakdown of the colloidal structure under the influence of gradient fluxes in the liquid medium†.

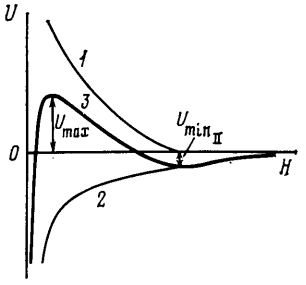


Figure 1. Potential curves for the interaction of two disperse particles: 1) repulsive curve; 2) attractive curve; 3) resultant curve in the presence of a repulsion barrier U_{max} and a secondary minimum with a depth $U_{min\,II}$ (U is the potential energy of the interaction of the particles and H the distance between them).

†A change in viscosity is also possible as a consequence of the orientation of the anisometric micro-objects in the stream, but these effects are comparatively small and will not be considered here[1-4].

The magnitude of the anomaly in the viscosity is determined by the change in the stability of the structure in the deformation process. The stability of a thixotropic system depends in its turn on the binding energy between its constituent elements and correspondingly on the depth of the secondary minimum on the potential interaction curves (Figs.1 and 2).[5]

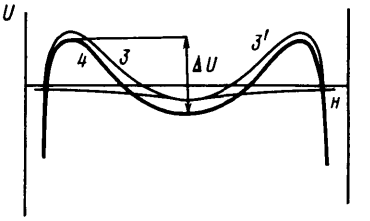


Figure 2. Potential curve for the interaction of a single test particle with two neighbouring particles (curve 4) in the presence of an energy minimum ΔU. Curves 3 and 3' are the resultant pair interaction curves.

The systems arising as a result of the fixation of micro-objects at the secondary minimum constitute periodic colloidal structures of the first type (PCS_1) with thixotropic properties. As a rule the PCS_1 are of a local character, i.e. they are not formed throughout the bulk of the system (under certain conditions and at a sufficiently high concentration in the solid phase, complete immobilisation of the dispersion is possible) and consist of ordered micro-regions (tactoids) alternating with individual "amorphous" sections with a lower density[6]. Such a tactoid structure, which is known for dispersions of many substances, particularly argillaceous minerals[7-10], is responsible for the possibility of the appearance of anomalies in viscosity, whose magnitude $\eta_0 - \eta_m$

(η_0 and η_m are the viscosities of the virtually undisrupted structure and the structure disrupted to the maximum extent) naturally depends on the depth of the potential minimum $U_{min\ II}$ (Fig.3)[1,11,12].

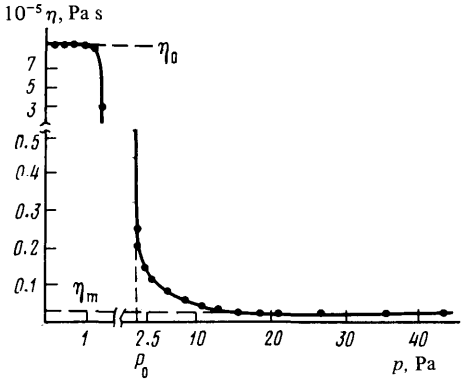


Figure 3. Dependence of the viscosity on the shear stress in a 10% aqueous (wt.%) dispersion of bentonite[11].

At the same time the authors of a number of studies[13-15] drew attention to the fact that the magnitude of the anomaly in viscosity does not determine the capacity of the system for thixotropic recovery and is not an unambiguous characteristic of thixotropic properties: thixotropy is defined as the isothermal and reversible sol ⇌ gel transformation[16,17]. One should bear in mind that many colloidal structures decompose irreversibly (partially or completely); complete reversibility is a rare case arising as a consequence of syneresis and other possible processes#. Fully irreversible PCS are not strictly speaking thixotropic systems. However, the origin, structure, and many properties, for example peptisability, are similar for reversible and irreversible PCS. Furthermore, both types of PCS undergo syneresis, which can be sharply accelerated due to external influences leading to the breakdown of the structure and can occur with partial or complete precipitation of the phase. However, there is a possibility of a microrecovery to some extent, which can be inferred solely on the basis of special studies.

Despite the large number of studies on thixotropy[1,5,6,11-27], little is known about the mechanism of the recovery processes, their energetics, and kinetics. Thus it is not clear which dispersions can recover their structure, to what extent, and over what period. One of the causes of this situation is apparently insufficient investigation of the structural transformations at the microlevel with determination of quantitative rules governing the interaction of micro-objects in external force fields. In a number of studies an attempt has been made at a quantitative interpretation of the thixotropic recovery on the basis of general equations, which are usually empirical (or semiempirical) (see, for example, Refs.23, 24, and 28-31). The results of the analysis of thixotropic multicomponent mixtures with allowance for the kinetics of the breakdown and recovery of the structural elements have been published[12,26]. A model of a thixotropic system, developed using the methods of hydrodynamics, rheology, and information theory as well as the mathematical apparatus of Markovian processes has been proposed[32]. The phenomenon of thixotropy has also been considered on the basis of the thermodynamics of irreversible processes[33,34].

It has been noted[14,35] that thixotropy can be of two kinds: based on stability and characterising the breakdown and recovery of the structural network, and based on viscosity and reflecting the breakdown and recovery of individual aggregates of colloidal particles.

Dilatancy, usually expressed by an increase of viscosity over a certain medium range of deformations, is, in addition to thixotropy, also a characteristic rheological property of colloidal dispersions (Fig.4). Dilatancy frequently plays an important role in industrial and natural processes. Dilatant effects frequently hinder the technology and transport of dispersions and limit the intensification of deformation processes[6,36-41]. Dilatant rocks (various types of earth, soil, etc.), whose rheology is of interest to many specialists, are widely distributed in nature; dilatancy has a major influence on the behaviour of these rocks (for example, in different instances of "stabilisation" of clay ground[42], in the treatment of soils[43], in different rheological processes, etc.). At the same time the causes of the onset of the dilatant flow regime have been inadequately determined and the existing explanations are not unique[5,6,15,36,44-46].

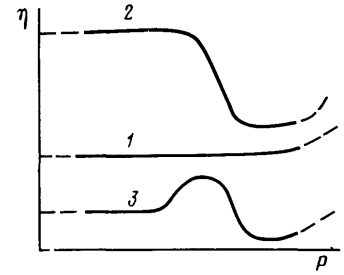


Figure 4. Dependence of the viscosity on the shear stress for different systems: 1) pseudoplastic (Bingham); 2) structural-viscous (thixotropic); 3) dilatant.

II. THE PROBLEM OF THE DILATANCY OF DISPERSIONS WITH MODERATE AND LOW CONCENTRATIONS OF THE SOLID PHASE

According to the literature[47-49], dilatancy (dilatation) is defined as a homogeneous deformation involving the volume expansion of highly concentrated dispersed systems. The expansion of such dispersions is caused by the fact that, with increase in the rate of shear, the particles pass into a less close-packed state generating pores which suck in the liquid: the volume of the system then increases and the dissipation of energy is enhanced. This is observed particularly clearly in pastes where the dispersed particles are almost close-packed. On deformation, the particles move away from one another (some approach one another), which

#Various binding mixtures, in which solidification processes take place, increasing the stability and the possibility of its restoration after the breakdown of the structure of the mixture, are frequently classified as reversible systems. In this case the term "reversibility" naturally has a limited significance.

leads to an increase of volume[6,21,50-52]. The volume of many disperse systems with close-packed particles changes on deformation regardless of whether the gaps between the particles are filled with water or air[51]. The viscosity and volume of certain concentrated dispersions increase as the rate of shear is altered, although there is in all probability no direct contact between their colloidal particles[53,54].

However, dilatant phenomena are more varied than would follow from the concept of dilatancy as deformation of volume expansion[48-50]. From the standpoint of these ideas, it is difficult to explain rheological data such as the absence of expansion in the dilatant deformation regime, for example, in starch pastes[52]; some workers believe that an increase of volume in dilatancy is altogether non-obligatory[21]. Furthermore, dilatancy has been observed in many dispersions containing the solid phase in an amount much smaller than would correspond to close-packing.

The range of compositions of dilatant dispersions is very wide. Thus, starting from systems concentrated to the limiting extent, for example, hydro-dispersions of silica or quartz glass (with a volume fraction of the solid phase $\phi = 0.85-0.87$),[55,56] the following systems are dilatant: dispersions of alumina in water (0.60) [56] and of iron in carbon tetrachloride (0.46),[57] aqueous clay strata (0.40–0.47),[58] quartz (0.41–0.45),[59] and starch (0.38–0.48),[56,59] dispersions in liquids of different kinds, latices (0.30–0.50),[44,45,60-62] titanium dioxide (0.30–0.43),[63,64] barium sulphate and carbonate (0.30),[65] latex PCS (0.12–0.40),[66-68] etc.

The above features—dilatancy of colloidal structures with a low content of the disperse phase and the absence of expansion on shear—led to the postulation of various mechanisms of dilatancy (more precisely of the increase of viscosity on shear) in dispersions with high and low concentrations[15,44,45,51,53,61,69-71]. Different terms have been proposed for the deformation of the latter systems: "quasi-dilatancy"[44,61], "pseudo-dilatancy"[72], "antithixotropy"[73], "negative thixotropy"[74,75], etc., the term "dilatancy" being retained for processes consistent with the definition given above[47-50]. However, this terminology has not gained wide currency.

The complexity of the problem under discussion arises from the fact that the increase of viscosity on shear or, in other words, the increase of the resistance offered by the system to external influences may be a consequence of the occurrence of different (one or several simultaneous) comparatively little investigated processes (many of which are reversible), rather than of the absence of a unified terminology; this greatly hinders the determination of the real mechanism responsible for the behaviour of the system under deformation conditions. We may note the following processes.

1. Reversible deformation of a highly concentrated dispersion accompanied by an increase of the viscosity and volume of the system (the Reynolds and Reiner dilatation[47-49]).

2. Reversible deformation of dispersions at moderate and low concentrations accompanied by an increase in viscosity at constant volume (quasi-dilatancy as defined by Krasheninnikov and coworkers[44,61]).

3. Rheopey—acceleration of the restoration of the thixotropic structure disrupted beforehand (as defined by Freundlich and Yuliusburger[76]).

4. Long-range aggregation (long-range coagulation) with fixation of micro-objects at the secondary potential minimum as well as short-range coagulation (fixation at the primary minimum) induced by the flow (Fig.5).[5,77-85] The statistical theory of aggregation under the conditions of steady-state flow has been developed[86].

5. Stabilisation of the dispersion as a result of unidirectional and periodic deformations and their superposition[14,87-89] as well as vibro-treatment[90-92]. It has been noted[89] that, depending on the rate of shear or the frequency of sinusoidal vibrations of a kaolin hydrodispersion, either thixotropic or dilatant effects arise in the latter. An increase of the rate of shear with the same stress under the conditions of the superposition of two types of deformation can arise in flow through tubes as a consequence of the appearance of random sources of vibrations. It has been concluded[92] that the capacity for thixotropic transformations of a dispersion compacted by vibro-treatment increases with increasing density of the medium. However, the increase of viscosity with increasing density of the medium greatly exceeds its decrease due to the thixotropic breakdown. The characteristics of the formation and breakdown of dispersed structures under the conditions of the joint action of vibration and surfactant additives have been discussed[93].

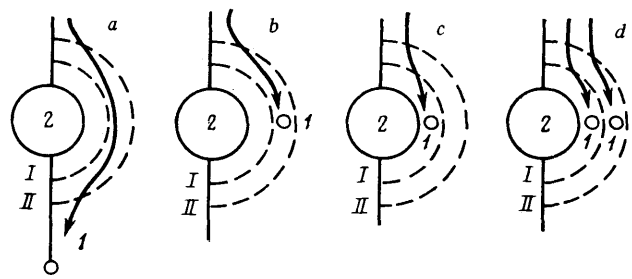


Figure 5. Schematic illustration of the interaction of micro-objects in a flow: *a*) no bond formed between particles *1* and *2*; *b*) particle *1* fixed at the secondary (II) minimum; *c*) particle *1* fixed at the primary (I) minimum; *d*) particles *1* fixed at the primary and secondary minima[80].



Figure 6. Electron micrograph of the aggregation of rod-shaped sepiolite particles having electrical dipole moments[94].

6. Stabilisation of the colloidal structure as a result of its rearrangement under the influence of the flow. For example, the structure comprising non-uniformly arranged particles can become stabilised after the particles have been more uniformly distributed, or the strength of the bonds between anisometric particles—rods and plates with permanent electric dipole moments—can increase under the influence

of hydrodynamic forces which is apparently characteristic of dispersions of argillaceous minerals (Fig.6).[5,81,94-99]

7. The fluidity of a dispersion can diminish following the onset of turbulence, which can be interpreted as an increase of viscosity[100-103]; this is by no means always easy to observe, particularly for an anomalously microturbulent regime and also in the presence of aggregation processes[104].

Furthermore, considerations have been put forward concerning the possibility of other processes leading to the stabilisation of the system. It has been suggested[105] that the elasticity of dispersions of gas carbon black in a mineral oil is determined by the breakdown of the network of carbon black particles with formation of chain fragments; the formation of the coagulation network and the rearrangement of its structure in dilatancy has been indicated in a number of studies. Many investigators have noted the need to take account of the interaction forces, the solvation effects, and other factors which can influence the flow regime. Despite the importance of such explanations, they are nevertheless largely hypothetical and are usually one-sided.

The determination of the mechanisms of processes occurring in disperse systems subjected to external force fields is an extremely complex problem whose solution solely with the aid of rheological methods, without a detailed description of the system, as a rule involves considerable difficulties. As a result of failure to take into account this factor adequately, a heterogeneous rheological terminology has arisen[14,15,70,88,90]; there have been frequent instances of the incorrect employment of different terms, which has been discussed in a number of studies[13-15,70,99,106], as well as others. Thus the term "rheopexy"[107,108] has apparently been used (in conflict with the definition of Freundlich and Yuliusburger[76]) to denote a dilatant increase in the viscosity of the dispersion§; the increase of the viscosity of a surfactant solution with a simultaneous alteration of pH has been called a rheopectic increase[109]. The changes in the viscosity of a polymer solution under the influence of shear deformation are frequently referred to as thixotropic (Refs.110, 111, etc.), which cannot be regarded as correct.

Processes in which the stability or viscosity of the system decreases are frequently classified as thixotropic, although in terms of their mechanisms they can be very remote from thixotropy[106]. As an example, one may quote the decrease of the elastic properties of a polymer solution following the rupture of the three-dimensional network arising as a consequence of the chemical "cross-linking" of the chain, as well as the disruption of gel monolith (swollen fibre, hydrated sorbent, etc.). A different significance is frequently imparted to the concept of colloidal structures in rheological studies; attention has been drawn[71,81] to the insufficiently clear-cut nature of the term "coagulation structures", which does not reflect the entire wide variety of different types of dispersions[5,81,99,112,113].

The inadequate investigation of dilatancy phenomena precludes a sufficiently complete explanation of the fundamental experimental data. For example, it is not clear what determines the difference between the volume of a close-packed disperse phase and its volume under conditions where dilatant flow begins; this difference can be small in some cases[56,114], while in others it can be very significant[57,65-68,115]. Furthermore, the question arises why dilatancy is manifested in poly(vinyl chloride) plastisols ($\phi = 0.5$) for particles of one size, while in the presence of particles of two sizes there is no dilatancy[116]; the dilatancy of paint and varnish systems based on TiO_2 disappears at 50 °C,[64] while in the case of quartz glass dispersions it disappears at 80 °C.[117]

Studies have been published recently on the rheological properties of PCS. It was found that PCS_2 (with a limited volume of the medium) at moderate and low concentrations are of the dilatant type under certain conditions in contrast to PCS_1 which are pseudoplastics. A detailed quantitative characterisation of these dispersions permitted an interpretation, somewhat different to the previous one, of the deformation processes and the establishment of the overall factors which determine the onset of a dilatant regime in various systems.

III. DILATANT-THIXOTROPIC TRANSFORMATIONS OF PERIODIC COLLOIDAL STRUCTURES

The differences between the PCS of different types are determined by the nature and forces of the interaction between micro-objects[5,81]. The PCS_1, which have arisen as a consequence of the predominance of attraction forces over long distances, are thixotropic systems which are both reversible and partly or completely irreversible. A second type of periodic colloidal structures (PCS_2), with a limited volume of the dispersion medium, is characterised by the predominance of repulsion forces over attraction forces, i.e. in the PCS_2 the dispersed particles interact under "constrained" conditions, which determines the large-scale nature of the order. Therefore, the PCS_2 fill almost the entire volume and their quasi-crystallinity is frequently readily indicated by their rainbow colour[118]. The constrained conditions play an important role in the behaviour of dispersions: ease of peptisation, liquefaction following the addition of a small amount of electrolyte, and conversion into thixotropic PCS_1 on addition of a further amount of the electrolyte (Fig.7) are characteristic of PCS_2.[5] The PCS_2—dispersions stabilised by the presence of double ionic layers (DIL) or adsorption-solvate layers (ASL)—have dilatant properties [this has been established in a study of aqueous dispersions of polyacrylonitrile (PAN) [66-68,119] and Al_2O_3 (Refs.120–123 and others)].

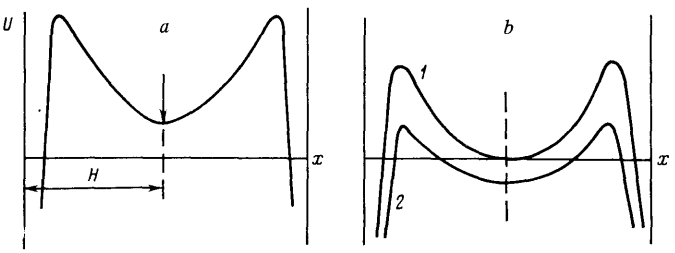


Figure 7, Potential curves for the interaction of particles: *a*) in the presence of a low content of electrolyte—in PCS_2; *b*) with increase of the content of electrolyte—in PCS of an intermediate type (curve *1*) and in PCS_1 (curve *2*).

§ It has been suggested[15,70] that the anomalous increase of viscosity on shear deformation without an increase in the volume of the system be called kinepexy (instead of quasi- or pseudo-dilatancy, antithixotropy, etc.).

PAN dispersions ($a \approx 150$ nm; ξ-potential of 40–52 mV), which are dilatant at low NaCl concentrations (0.004–0.024 M) and thixotropic at moderate concentrations (0.024–0.035 M), belong to stable ion-stabilised systems in terms of the nature

of the sedimentation and the magnitude of the charge (Fig.8). Figs.9 and 10 present plots of the function $I/\tau = f(P)$, where τ is the time of the movement of the sphere in the cylinder of the viscometer and P is the applied load. Evidently, with decrease of the NaCl content or with increase of the PAN concentration, the dilatant section begins at lower flow rates and for higher loads. This is due to the increase of the specific effective volume (fraction) of the disperse phase ϕ_e, which includes its real volume ϕ and the volume of the surface layers ϕ_S (immobilised as a consequence of the formation of DIL or ASL on the surface of the particles). An increase of ϕ_e leads to a decrease of the effective free or vacant volume ϕ_V:

$$\varphi_v = 1 - \varphi_e = 1 - (\varphi + \varphi_s) \quad (1)$$

or

$$\varphi_v = \varphi_0 - \varphi_s , \quad (2)$$

where $\phi_0 = 1 - \phi = \phi_V + \phi_S$ is the volume fraction of the liquid medium including the volume of the surface layers (DIL or ASL). The decrease of ϕ_V (as a consequence of the increase of ϕ_S due to the decrease of c_{NaCl} and the expansion of the DIL or the increase of ϕ with increase of the PAN content) leads to a greater constraint on the movement of the particles, which hinders the relaxation of the stresses arising in the system. Therefore the smaller the value of ϕ_V, the lower the rates at which dilatancy begins and at the same time a greater force is required for deformation (other conditions being equal).

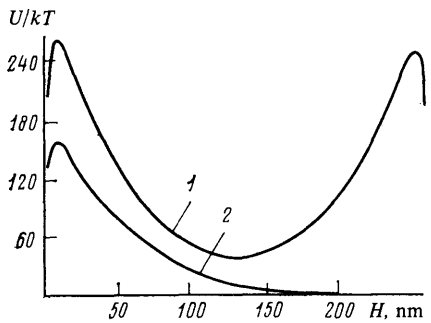


Figure 8. Potential curves for the interaction of PAN particles (for a volume concentration of the disperse phase $\phi = 0.25$) involving three particles with $\zeta = 52$ mV (curve *1*); for two particles with $\zeta = 41$ mV (curve *2*).

The fraction of "free" critical volume corresponding to the onset of the dilatant regime can be designated by $\phi_{V,cr}$. Then

$$\varphi_{v,cr} = 1 - \varphi_{e,cr} = 1 - (\varphi_{cr} + \varphi_{s,cr}) \quad (3)$$

or

$$\varphi_{v,cr} = \varphi_{0,cr} - \varphi_{s,cr} , \quad (4)$$

The above components of the volume fractions are illustrated in the schemes for model PCS_2 (Fig.11). Evidently the quantity $\phi_{e,cr} = 1 - \phi_{V,cr}$ should be approximately equal to the degree of saturation of the volume of the system by the solid phase for close-packed disperse particles in the absence of ionic and solvation layers, i.e. when $\phi_S = 0$ and

$$\varphi_{v,cr} = \varphi_{0,cr} = 1 - \varphi_{cr} . \quad (5)$$

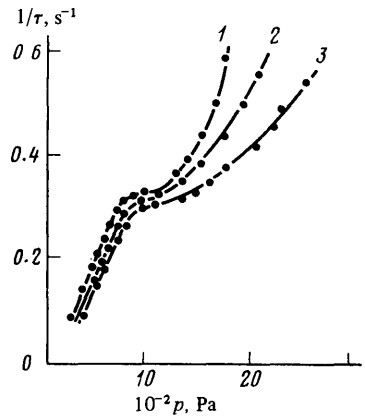


Figure 9. Dependence of the rate of deformation on the shear stress in aqueous PAN dispersions ($\phi = 0.165$) at 18 °C and different NaCl concentrations (M): 1) 0.020; 2) 0.014; 3) 0.004.

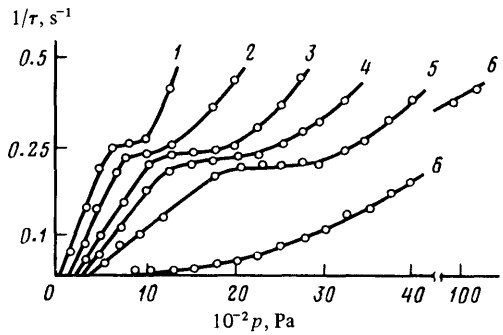


Figure 10. Dependence of the rate of deformation on the shear stress in aqueous PAN dispersions at 18 °C and different NaCl concentrations [1)–3) 0.024 M; 4) and 5) 0.005 M] and for different PAN volume fractions [1) 0.127; 2) 0.196; 3) 0.224; 4) 0.351; 5) 0.387; 6) 0.455].

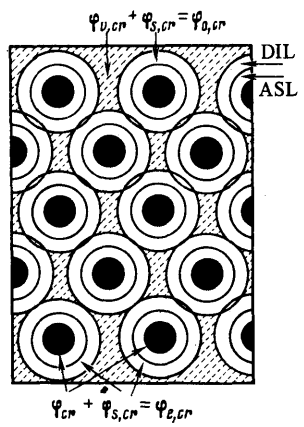


Figure 11. The periodic colloidal structure (PCS_2) stabilised by a double ionic layer. The effective volume (fraction) of the disperse phase and the "free" volume have critical values.

It follows from the above relations between the volume fractions [Eqns.(1)–(5)] that the differences between the critical concentrations of the disperse phase in different instances of deformation are caused mainly by the influence of the DIL and ASL, whose volume fraction $\phi_{s,cr}$ increases the volume fraction of the solid phase ϕ_{cr} to $\phi_{e,cr}$—the effective degree of volume saturation in "close" packing. In this case

$$\varphi_{e,cr} \simeq \varphi_{cr} + \varphi_{s,cr} . \qquad (6)$$

Thus the critical effective volume $\phi_{e,cr}$ is equivalent to the volume of the close-packed solid phase corresponding to the appearance of dilatancy; the quantity $\phi_{e,cr}$ then represents the sum of the critical volumes of the solid phase (ϕ_{cr}) and the protective layers ($\phi_{s,cr}$)(ASL and DIL) or, in other words, $\phi_{e,cr}$ is the effective hydrodynamic volume of the disperse phase.

The value of $\phi_{e,cr}$ for an ion-stabilised dispersion (Fig.11) can be determined with some approximation by plotting potential curves by the method of Efremov and coworkers[5,124] or analytically[125,126]. However, in order to obtain the true value of $\phi_{e,cr}$ for which the dilatant regime is established, it is necessary to take into account the relaxation times of the DIL and the entire disperse system, which is difficult. The DIL relaxation is known to be comparatively rapid[127]¶, but this applies also to DIL in the absence of structured boundary liquid layers, which can determine to a large extent the characteristic features of the rheological behaviour of concentrated dispersions—their structural-viscous properties.

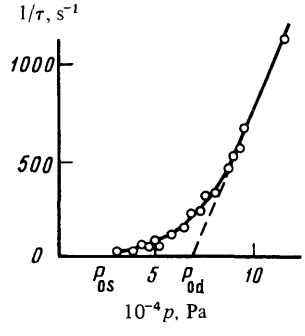


Figure 12. Dependence of the rate of deformation on the shear stress in an aqueous PAN dispersion (ϕ = 0.485) at an NaCl concentration of 0.005 M; P_{0S} = static limiting shear stress; P_{0d} = dynamic limiting shear stress.

The upper concentration limit, corresponding to the disappearance of dilatancy and the onset of structural-viscous flow (Fig.12), is therefore apparently determined by the long relaxation times of the system as a consequence of the decrease in the thickness of the liquid layers ($\phi_v \to$ min when $\phi \to$ max), the overlap of the compressed DIL, and the decrease of the depth of the energy well (Fig.13), which intensifies the aggregation and coagulation processes. The rupture of the bonds between particles undergoing rearrangement on deformation requires the application of appreciable loads. The system then behaves like thixotropic highly viscous PCS_1, which corresponds to the curve in Fig.12.

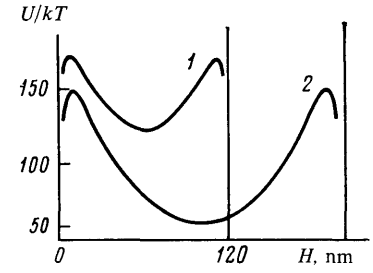


Figure 13. Potential curves for the interaction of the particles of aqueous PAN dispersions: 1) ϕ = 0.415 (distance between the surfaces $H_1 \cong$ 60 nm); 2) ϕ = 0.30 ($H_2 \cong$ 100 nm).[119]

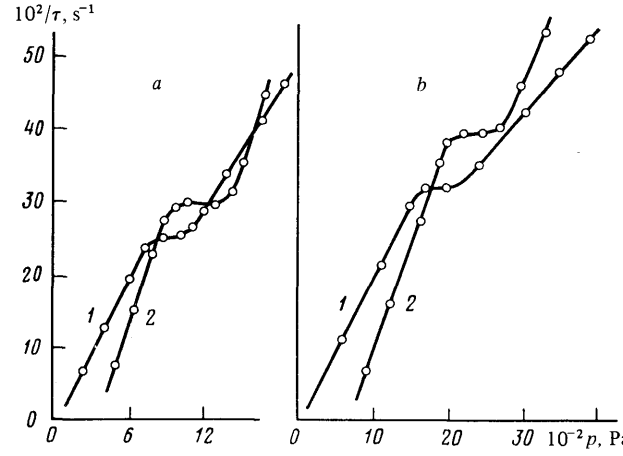


Figure 14. Dependence of the rate of deformation on the shear stress in aqueous PAN dispersions for c_{NaCl} = 0.22 M: *a*) ϕ_1 = 0.15 at 20 °C (curve *1*) and 68 °C (curve *2*); *b*) ϕ_2 = 0.25 at 10 °C (curve *1*) and 50 °C (curve *2*).[46]

With increase of temperature, the dilatant sections of the rheological curves for PAN dispersions shift to the region of higher rates of shear and a greater applied load (Fig.14). It is evident that (a), at a comparatively high temperature (68 °C) and a low PAN concentration (ϕ_1 = 0.15), the dilatant regime is shown fairly clearly as a consequence of the characteristics of the ionic stabilisation (a greater DIL thickness in the presence of a low content of ions and the retention of ionic stabilisation at elevated temperatures) and that (b) an increase of the PAN content shifts the dilatant section (like an increase of temperature) to the region of high rates of shear and a greater applied load.

¶ The DIL relaxation time θ is a function of the system parameters. Under the usual conditions, θ for a given solvent and electrolyte depends only on the concentration c_{el}. Thus, for an aqueous solution at the usual temperature $\theta \cong 10^{-10}/c_{el}$; when $c_{el} = 10^{-3}$ *N*, we have $\theta \cong 10^{-7}$ s.[127]

Interesting results have been obtained[120–123] in the study of aqueous dispersions of two fractions, I and II, of Al_2O_3 (with effective particle diameters of 4 and 40 μm and a nearly ellipsodal particle shape with an axial ratio of 1 : 3). The dispersion medium was a solution of sodium carboxymethylcellulose (0.1 wt.%); at pH 9.5 the particles had a ξ-potential of approximately −140 mV. Plots of potential curves for the interaction of the particles of the highly disperse Al_2O_3 system with $\phi \cong 0.50$ showed that it is a PCS_2 system in which repulsive forces predominate between the particles (separated by an average distance of 35 nm). The dispersion of large Al_2O_3 particles, fixed at the secondary potential minimum, is a thixotropic PCS_1. The study of the rheological properties of these systems reveals the following features.

1. The highly disperse PCS_2 (fraction I) has dilatant properties (Fig.15, curve *1*) due to the constrained conditions in the interaction of the particles.

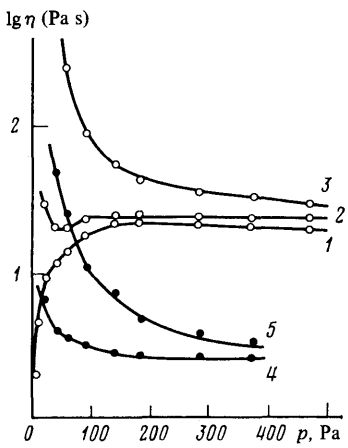


Figure 15. Rheological curves for Al_2O_3 dispersions characterising the change in the type of PCS as a function of the degree of dispersion of the solid phase and the KCl concentration (M): 1) 0; 2) 0.08; 3) 0.25 (fraction I); 4) 0; 5) 0.25 (fraction II).[122]

2. When small amounts of KCl are introduced into the PCS_2, the dilatant properties degenerate and the deformation regime becomes close to a Newtonian regime. A further addition of the electrolyte causes (in conformity with Fig.7) the conversion of the PCS_2 into the thixotropic PCS_1 (Fig.15, curves *2* and *3*).

3. When an electrolyte is introduced into the thixotropic PCS_1, formed by fraction II, with a low degree of dispersion, the latter is stabilised as a consequence of the increase in the depth of the minimum (Fig.15, curves *4* and *5*).

4. The dilatant regime in the deformation of the PCS_2 passes to a structural-viscous (thixotropic) regime when the disperse composition of the system is altered by adding to the latter fraction II, with a low degree of dispersion, instead of the same mass of fraction I (Fig.16). The transition $PCS_2 \rightarrow PCS_1$ then takes place and complex higher-order structures are formed (Fig.17);[99,128] in the latter the interaction of the large central particle with small particles can be illustrated by the periodic potential curve (Fig.18).[129] The breakdown of these complex aggregates under an external influence determines the structural-viscous deformation regime.

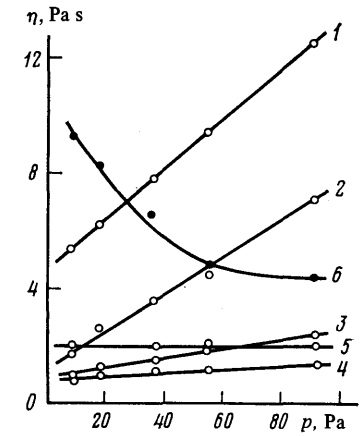


Figure 16. Flow curves for Al_2O_3 dispersions ($\phi \cong 0.50$) corresponding to different weight ratios of the fractions (I/II): 1) 80/20; 2) 70/30; 3) 50/50; 4) 40/60; 5) 20/80; 6) 10/90.[121]

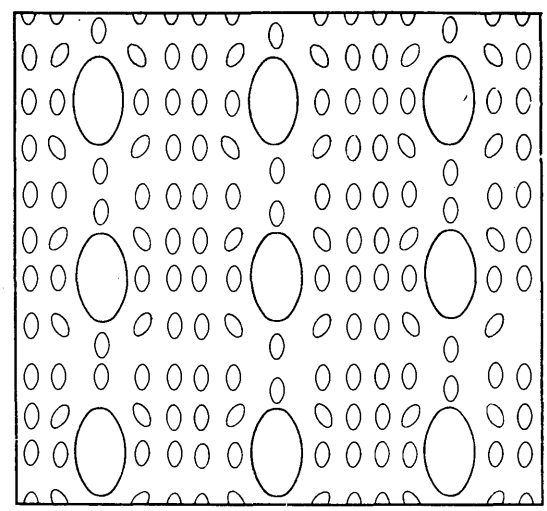


Figure 17. An element of a complex periodic colloidal structure consisting of large and small particles.

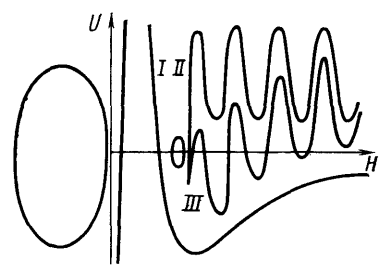


Figure 18. Potential curves characterising the interaction of small ellipsoidal particles with a large ellipsoidal particle: I) curve for the pair interaction of the particles; II) periodic curve for the interaction of several small particles in the absence of a large particle; III) overall curve for the interaction of heterogeneous particles.

5. The dilatant deformation regime in PCS_2 also passes to the structural-viscous regime after the introduction into the system of 1–2 wt.% of Latnensk clay (or a modified aerosil) instead of the corresponding amount of Al_2O_3 (Fig.19).[121] The considerable stabilisation of the dispersion after the introduction of the clay may be a consequence of the aggregation of heterogeneous particles, particularly when account is taken of the possibility that the clay particles have a permanent electric dipole moment[5,99]. The breakdown of these aggregates can lead to the structural-viscous deformation regime.

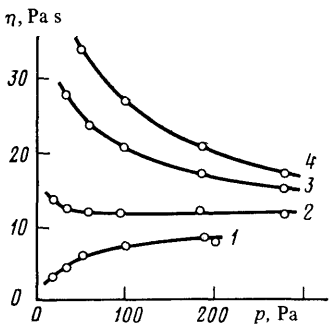


Figure 19. The influence of added Latnensk clay (instead of the corresponding amount of Al_2O_3) on the flow of Al_2O_3 dispersions (fraction I); percentage of clay (%): 1) 0; 2) 1.0; 3) 1.5; 4) 2.0.[121]

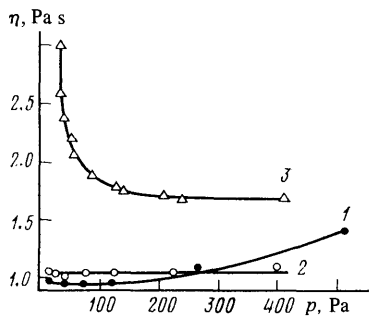


Figure 20. Dependence of the viscosity of aluminium hydroxide dispersions on the shear stress at different aluminium oxide nitrate concentrations (g litre^{-1}): 1) 16; 2) 60; 3) 100.[130]

Tikhonov and coworkers[121–123] showed for the first time that the rheology of dispersions is determined by their stability and hence by the conditions and the nature of the interaction forces between micro-objects: dilatant properties are manifested primarily in systems resistant to aggregation, under constrained conditions, while structural-viscous plastic properties are characteristic of less stable thixotropic dispersions.

The results of the study of dispersions of aluminium hydroxide in aqueous solutions of aluminium oxide nitrate have been published[130]. The content of the solid phase was 64% (ϕ = 0.64) in dispersions (1) and (3) and 62% (ϕ = 0.62) in dispersion (2). The shape of the colloidal particles (average diameter ~1 μm) was nearly spherical. In the presence of a low content of aluminium oxynitrate, the $Al(OH)_3$ dispersions are resistant to aggregation and exhibit dilatancy (Fig.20, curve *1*); with increase of the content of ions, there is a transition from the dilatant flow regime to the Newtonian regime and further to the structural-viscous regime, i.e. the $PCS_2 \rightarrow PCS_1$ transformation takes place (Fig.20, curves *2* and *3*). An increase of temperature causes the liquefaction of the system (as for PAN dispersions).

A transition of dilatant dispersions (ϕ = 0.48) of poly(methyl methacrylate) (PMMA) in dibutyl phthalate (DBP) to thixotropic structural-viscous systems on successive replacement of DBP by dioctyl sebacate (DOS) has been demonstrated[131] (Fig.21). The authors[131] explained this by the difference between the solvating properties of DBP and DOS, with which one can in the main agree, although the question of the role of the double ionic layers (DIL), which can significantly affect (together with solvation) the behaviour of dispersions, particularly in the region of high DOS concentrations, remains open. However, there can be hardly any doubt that the $PCS_2 \rightarrow PCS_1$ transition occurs in this instance.

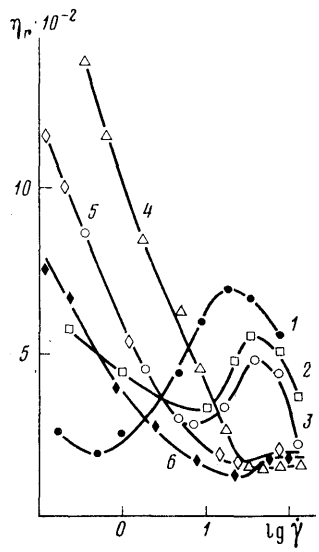


Figure 21. Dependence of the relative viscosity of a PMMA dispersion in DBP, DOS, and their mixtures on the rate of shear. DOS content (vol.%): 1) 0; 2) 10; 3) 20; 4) 40; 5) 70; 6) 100.[131]

IV. FACTORS DETERMINING THE DILATANT DEFORMATION REGIME

In the introduction it was noted that many investigators have pointed out various factors which in their view are responsible for the appearance of dilatancy on deformation of various dispersions. Consideration of these factors leads to the conclusion, that despite the significant differences in the nature and type of their influence, their action reduces ultimately to a decrease of the "free" volume ϕ_v of the system and to a greater retardation of the relaxation processes. It is then found that the results obtained in

the study of PCS, which were described in the preceding section, are of general significance and their use in rheological research is of definite interest. We shall consider the principal factors to which the majority of investigators refer when they explain the mechanism of the appearance of dilatant flow conditions.

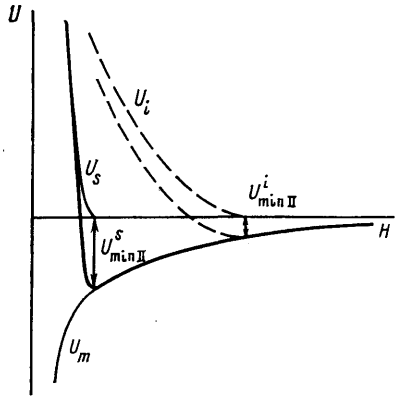


Figure 22. Potential pair interaction curves; $U^S_{min\ II}$—secondary minimum due to the presence of solvate layers on the surface; $U_S(H)$—repulsion energy curve for these layers; $U^i_{min\ II}$—secondary minimum due to the predominance of the attraction energy over long distances [$U_m(H)$ curve] over the double ionic layer repulsion energy [the $U_i(H)$ curve][99].

1. Adsorption-solvate Layers

It has been established[69] that dispersions (ϕ = 0.48) of the acrylonitrile–methacrylate copolymer in 1-propanol, 2-nitro-1-propyl acetate, and 2-nitro-1-butyl acetate are viscoplastic, while dispersions of the same copolymer in 2-nitro-1-propanol and 2-nitro-1-butanol are dilatant. The authors[69] explain the dilatancy by solvation and by the unusual behaviour of hydrogen bonds; at the same time they also postulate that the breakdown of the aggregates of the disperse particles formed at rest and the formation of coagulation structures should likewise give rise to dilatancy. Naturally, in viscoplastic dispersions the lower degree of solvation may be responsible for their structure being analogous to that of PCS_1. On the other hand, the more stable solvate layers, which might have been influenced by hydrogen bonds, can (when their thickness h is sufficiently great) lead to constrained conditions—a decrease of ϕ_V and the formation of dilatant PCS_2. This agrees with the fact that boundary liquid layers with retarded relaxation can impart a high viscosity to a system under constrained conditions. However, a final conclusion requires the experimental detection of these layers and the determination of the role of DIL, which should exist on the surface of the polymer particles and should also exert a stabilising effect and correspondingly diminish ϕ_V.

The rheology of PMMA dispersions in dilute poly(vinyl chloride) solutions and in dialkyl phthalates has been investigated[132,133]. It was shown that thixotropic behaviour is characteristic of dispersions with weak solvation and adsorption effects; on the other hand, the onset of dilatancy is associated with a fairly pronounced manifestation of these effects and also depends to some extent on the viscosity of the dispersion medium. A dilatant latex dispersion at rest has been considered[45] as a system of non-interacting swollen micro-objects separated by a structural-mechanical barrier. For fairly large shear stresses, capable of deforming layers of the swollen polymer and of overcoming the repulsion forces, a structural network arises, being deformed after the cessation of external influences. It has been concluded that, with increasing degree of lyophilicity, polymer dispersions pass from the thixotropic to the dilatant state (in other words, the $PCS_1 \rightarrow PCS_2$ transformation takes place). Thus, by altering the interaction at the polymer–plasticiser interface and by creating the optimum structure of the swollen layer on the surface of the polymer particles, it is possible to impart dilatant properties to the system. The decisive importance of solvation and adsorption in the dilatancy of dispersions has also been discussed in a number of other studies[63,64,134–137].

It has been established[63,64] that TiO_2 dispersions (ϕ = 30–42%) in white spirit possess thixotropic or dilatant properties depending on the content of alkyd resins: the dispersions are thixotropic for c_{SA} = 2–5% and dilatant for c_{SA} = 7.5%, where c_{SA} is the concentration of the surfactant. Thus the comparatively thin adsorption layer of the surfactant apparently determines the interaction of the TiO_2 particles over a long distance with formation of PCS_1 (Fig.22);[99] thicker and highly viscous layers lead to constrained conditions and PCS_2, whose electrical conductivity is smaller by several orders of magnitude than that of PCS_1. The fact that dilatancy disappears at temperature up to 50 °C or with increase in the solvent power of the solvent constitutes an important confirmation of the validity of the postulate that the ASL play a decisive role in imparting dilatant properties to TiO_2 dispersions; ion-stabilised PCS_2 retain dilatancy at relatively higher temperatures[138]. A sharp decrease of the dilatancy of starch dispersions (ϕ = 0.48) with increase of temperature has been observed[117,139], while the dilatancy of an aqueous dispersion of quartz glass (ϕ = 0.77) disappears only at 80 °C. The ζ-potential is ~|30| mV for quartz particles in an aqueous medium at pH 5.0;[134] consequently the dispersion was in all probability an ion-stabilised PCS_2.

The influence of the adsorption layer of the surfactant on the effective volume fraction of the disperse phase for a small thickness of the layer h, i.e. $h/a \ll 1$,[140,141] has been taken into account with the aid of the following expression:

$$\varphi_e \approx \varphi(1+3\,h/a)\,, \qquad (7)$$

where ϕ is the volume fraction of the solid phase, h the thickness of the surfactant layer, and a the radius of the particles.

2. Double Ionic Layers

In view of their wide occurrence, DIL frequency exert a decisive influence on the onset of the dilatant deformation regime. This has been confirmed in the studies quoted in the previous section as well as a number of others. Thus the influence of the concentration of the dilute electrolyte, the nature and pH of the liquid medium, and the size and concentration of the disperse SiO_2 particles on the nature of the deformation of the system, has been studied in detail[134]. The determination of the sedimentation volumes and of the ζ-potential made it possible to describe the stabilisation of the particles and to find the effective volume of the disperse phase ϕ_e and its ionic-electrostatic and solvation constituents.

This resulted in an explanation of the deviation of the rheology of SiO_2 dispersions from Newtonian behaviour corresponding to the Einstein equation

$$\eta=\eta_0(1+2.5\varphi), \quad (8)$$

where η and η_0 are the viscosities of the dispersion and of the dispersion medium and ϕ is the volume fraction of the disperse phase.

Depending on the system parameters and the flow regime, SiO_2 dispersions had thixotropic or dilatant properties, which was explained by the electroviscous effect, i.e. by the influence of the DIL on the deformation process, and also by the presence on the surface of the particles of a solvate layer with a thickness h. The value of h was found graphically[134] using Eqn.(8) in the form

$$\eta_{sp}=2.5\ \varphi_e=k\varphi\ . \quad (9)$$

From Eqn.(9), it is possible to obtain the expression†

$$\frac{k}{2.5}=\frac{\varphi_e}{\varphi}=\frac{\pi(a+h)^3}{\pi a^3}=\left(1+\frac{h}{a}\right)^3, \quad (10)$$

where a is the radius of the disperse particles. As mentioned by Greenberg and Chang[134], the values of h were somewhat too low (1.5–1.7 nm).

The study of the viscous changes in a latex during dialysis led to the discovery of the so-called electroviscous effect, which consists in the fact that the viscosity of the latex increases by a factor of several hundreds as a result of dialysis and returns to its initial value after the addition of an electrolyte[142,143]. This reversible sol ⇌ gel transformation indicates the occurrence of the $PCS_2 \rightleftharpoons PCS_1$ transition, which takes place in the ion-stabilised latex as the concentration of ions is varied. It has been shown[144] that the density of the electric charge on the surface of latex particles and the ionic strength of the liquid medium have a significant influence on the rheology of dispersions as a consequence of the increase of the effective volume of the particles, which increases their hydrodynamic volume; the relation between the increment of the radius of the particles and the Debye parameter κ has been discussed.

Thus ASL and DIL are the main factors in dilatancy; their role reduces to increasing the effective volume of the disperse phase $\phi_e = \phi + \phi_S$ or, in other words, to decreasing the free volume of the system $\phi_V = 1 - \phi e$. When these layers are fairly large, constrained conditions appear even in dilute dispersions, in conformity with Eqn.(3).

The mechanism of the influence of ASL and DIL consists in the fact that, under constrained conditions, the displacement of the particles relative to one another on shear leads to the overlap of the layers and thei mutual repulsion, which gives rise to a stress whose relaxation depends on many system parameters. The ideas developed in relation to these phenomena have been confirmed by numerous experimental data and considerations put forward by various investigators. Thus a relation has been pointed out between dilatancy and (a) the free volume of the dispersion[56,62,145–151], (b) solvation and adsorption[36,40,45,63,64,131–137], (c) the double ionic layer, the ζ-potential, and the stability of colloidal particles[67,68,119,134,143–146,152–155], (d) the interaction of the particles and the formation of a bond[40,42,59,62,98,121–123,130,134–136,138,143,156–158], and (e) the superposition and repulsion of the ASL and DIL [63,64,121–123,135]; dilatancy has been explained in a number of studies by the dominant effect of repulsion forces[6,45,67,68,119,122,123,138,146,159]. Ideas concerning entropic repulsion have been envoked[45] (although apparently it would be more correct to employ the concept of osmotic pressure[160,161] or, in the general case, the concept of the disjoining pressure[5,81]).

The above principal results of studies designed to determine the factors governing dilatancy, which are by no means complete, are in good agreement with conclusions reached in numerous experimental and theoretical studies of the general characteristics of the rheological behaviour of colloidal structures under different conditions. In addition to the series of studies quoted above (for example Refs.54, 79, 80, 83, 134, 146, 152, etc.), we may also mention investigations[162–168] in which quantitative relations between the rheological and energetic parameters of dispersions have been discussed.

3. Peptisation

The peptisation of aggregates to individual disperse particles has the following consequences: (1) protective surface layers (ASL and DIL) arise on the fresh surfaces; (2) the thickness of liquid layers between the particles diminishes and the distribution of particles becomes more uniform; (3) the overall surface area of the particles increases; (4) the free volume of the dispersion ϕ_V diminishes. The deformation of dispersions unstable as regards aggregation can therefore entail the peptisation of the aggregates under the influence of shear forces[78] with formation of ASL and DIL of definite thickness, which should reduce sharply the values of ϕ_V. Thus peptisation is an important auxiliary factor in dilatancy. On the other hand, the main factors remain ASL and DIL in this case also, since only their formation diminishes the free volume and gives rise to constrained conditions. Naturally, in dispersions which are stable as regards aggregation, there will be either no peptisation at all or, under the influence of the flow, a reversible aggregation and deaggregation process may occur, which will be less pronounced the more stable the system[77–79].

The important role of peptisation and of the uniform distribution of particles in the manifestation of dilatancy in the deformation of various dispersions has been indicated[14,63,71,169–171]. It has been established[172] that weakly disperse suspensions of aggregates and individual PMMA latex particles (ϕ = 0.5) in DBP are dilatant (Fig.23), which has been explained tentatively by the orientation of the particles in the stream and by the formation of a new additional coagulation structure. One should apparently agree with the authors' claim[172] that the peptisation of aggregates of PMMA particles leads to the formation of PCS_2 (of an additional "coagulation" structure# according to Bubis et al.[172]), a decrease of ϕ_V, and the onset of dilatancy.

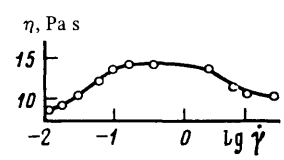


Figure 23. Dependence of the viscosity of a PMMA dispersion in DBP (ϕ = 0.50) on the shear velocity gradient[172].

†Series expansion of the cube of the sum and retention of only the first two terms for $h/a \ll 1$ yields Eqn.(7).

#It is erroneous to refer to colloidal structures of the PCS_2 as coagulation structures. The formation of PCS_2 is a forced process accompanied by an increase in the energy of the system[119].

At the same time the explanation of dilatancy is frequently restricted to a general postulate concerning "changes in the packing of coagulation structures"—network, chain, etc. structures. Thus it has been assumed[153] that the dispersion investigated consists of individual floccules in which colloidal particles form chains. In a shear flow the floccules combine with displacement of the particles from their equilibrium positions. A change in the packing of the particles on dilatancy with formation of a less ordered structure has been noted[145]. The authors of other investigations also believe that dilatancy results in the formation of various "coagulation structures", etc.

One cannot reject the possibility of aggregation and deaggregation processes in a flow[77-80,86], but the hypothesis of such processes must be adequately justified in each specific instance, which is as a rule difficult when rheological data alone are used. Therefore many investigators have endeavoured to employ various modern methods of physics and physical chemistry in rheological research. Here one must note the attempts at a quantitative description of the interparticle interaction forces[67,68,119-123,134,142,145,149], thermodynamic properties[33,34,83,86,137], and physicochemical characteristics[63,79,80,152,164,173] in systems undergoing deformation.

At the same time the modification and improvement of rheological methods are being continued. Methods based on unidirectional and periodic deformations and their superposition have been used[14,88,170,171] in the study of the structures of aerosil dispersions in organic and organosilicon liquids and also of aluminium naphthenate gels. It has been established that, under certain deformation conditions, the dependence of the dynamic modulus of shear G^{I} (the real component of the complex modulus $G^{\times} = G^{I} + iG^{II}$) on the extent of periodic deformation (on the sinusoidal regime) is characterised by a marked maximum; the increase in the stability of the system in this instance is explained by the transition of the coagulation structure as a result of peptisation to a more ordered state (i.e. by the $PCS_1 \rightarrow PCS_2$ transition). Similarly it has been observed[89] that 70% hydrodispersions of kaolin are thixotropic at low frequencies of sinusoidal oscillations and dilatant at high frequencies ($PCS_1 \rightarrow PCS_2$).

It was noted previously that dilatancy degenerates with increase of temperature. However, the results of different investigators have shown that, to a first approximation, there are two temperature ranges in which a dilatant regime passes to a Newtonian or structural-viscous regime. The first range (40–50 °C) corresponds to an appreciable breakdown and rearrangement of the ASL. Thus it has been established[63] that dilatancy of SiO_2 dispersions in solutions of alkyd resins in white spirit disappears below 50 °C as a consequence of the increasing solvent power of the solvent and the decreasing degree of adsorption of the resins. The second range (75–90 °C) corresponds to a sharp increase of the rate of relaxation of the DIL and of the stresses which have arisen as a result of the operation of external forces. The dilatant properties of concentrated aqueous dispersions of SiO_2 [117] and iron oxides[174] as well as, apparently, dilute ion-stabilised PAN latexes[67,68] disappear in this region. Naturally, other variants are also possible. It has been observed[175] that the relative viscosities of dilute bentonite suspensions depend little on temperature, while at high concentrations the viscosity increases appreciably and depends markedly on temperature, which has been explained by structure formation.

An attempt has been made[145,176] to devise a quantitative theory of the dilatant behaviour of dispersions by taking into account the van der Waals attraction forces, the DIL repulsion forces, and the external forces giving rise to shear deformation. A careful analysis of the dimensionless geometrical, energetic, and mechanical parameters of a dispersion undergoing deformation ($\phi = 0.65$) has been carried out[149]; equations describing the rheological properties of disperse systems which thicken and liquefy under the influence of shear deformations have been put forward. Rheological equations for thixotropic-dilatant structures have also been proposed[156,177]. The dependence of the relative viscosities of dispersions of spherical non-interacting particles on the volume fraction has been expressed[178] by the single-parameter equation

$$\eta = \left[1 + \frac{1.25\varphi}{1 - (\varphi/\varphi_{max})}\right]^2, \qquad (11)$$

where ϕ_{max} is the value of ϕ corresponding to close packing. In the presence of ASL or DIL on the surface, ϕ_e replaces ϕ and an equation of type (10) or, when the thickness of these layers is small, Eqn.(7) is used[178].

The following equation is employed for concentrated dispersions of glass spheres ($d \cong 27-118$ μm) in low-molecular-weight polyisobutylene[179]:

$$\eta_r = \left[1 + 0{,}75\left(\frac{\varphi/\varphi_{cr}}{1 - \varphi/\varphi_{cr}}\right)\right]^2. \qquad (12)$$

For monodisperse systems, $\phi_{cr} \cong 0.6$§ and for bimodal systems the dependence of the viscosity on the content of the smallest particles (at a constant overall concentration) passes through a minimum, which is related directly to the thixotropic and dilatant properties of the dispersions. An analogous relation has been observed in Refs.121, 180, 181, etc.

V. DILATANCY OF MICELLAR SOLUTIONS OF SURFACTANTS, SOAP GELS, AND SURFACE MONOLAYERS

Micellar solutions are known to be systems in thermodynamic equilibrium. The micelles have different shapes—usually spherical, cylindrical, or lamellar. The surface of cylindrical micelles is non-isotropic (has no circular symmetry), which can be accounted for by the unusual orientation of the dipolar molecules on the surface[113,182]. The micelles present in solution at not unduly high surfactant concentrations consist of hydrated surfactant molecules; there are comparatively thick liquid layers between the micelles[183].

The results of a study of the viscous properties of 1–15% aqueous solutions of dioctyl sulphosuccinate have been published[108]. At a concentration of 5% and above, the solutions prepared using distilled water are thixotropic (i.e. constitute a PCS_1). On the other hand, when inorganic electrolytes are present ($c_{el} = 1$ *N*), the viscosity of the system diminishes at low rates of deformation and increases at high rates. These rheological anomalies have been explained[138] by taking into account the salting-out effect of ions, which results in the formation of comparatively large micelles separated by hydrate layers (PCS_1), and the breakdown of large micelles into small ones at high rates of deformation, which leads to constrained conditions and the appearance of PCS_2. Thus the transition from the thixotropic to the dilatant flow regime observed in these solutions can be explained satisfactorily by the $PCS_1 \rightarrow PCS_2$ transition (Fig.24). Furthermore, under the conditions of salting-out in surfactant solutions, there is also a possibility of the preferential formation of extended instead of spherical micelles, which enhances the viscoelastic properties[184-186].

§ The value $\phi_{cr} \cong 0.6$ does not correspond to the close packing of monodisperse spheres ($\phi \cong 0.74$). This discrepancy is apparently due to the presence of ASL or DIL on the surfaces of the glass spheres [see Eqn.(6)].

The mechanism of the dilatant increase of viscosity in dilute solutions of hexadecyltrimethylammonium bromide in methylnaphthlene has been explained[187] by the appearance of a network of rod-shaped micelles under the influence of the flow. It has been suggested[138] that the network is formed from the very beginning of the deformation, but at low rates the rupture of the bonds between the micelles predominates (thixotropic liquefaction), while at higher rates the micelles themselves break down, which leads to constrained conditions and the formation of a PCS_2. These solutions have anomalous rheological properties at 22 °C, while at higher temperatures they become Newtonian liquids.

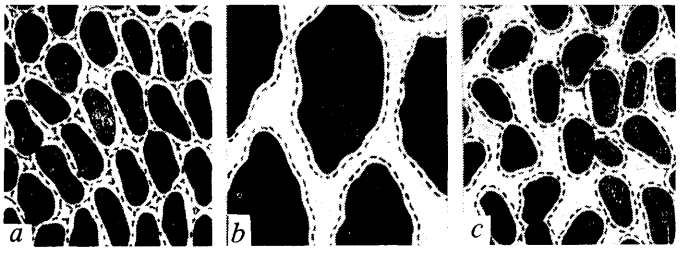


Figure 24. Schematic illustration of the changes in the micellar structure of surfactant solutions after the addition of an electrolyte ($a \rightarrow b$) and with increase of the rate of shear deformation ($b \rightarrow c$).

(a) Dilatancy of Soap Gels

Dilatant thickening has been observed in ammonium oleate[188] and organo-aluminium salt[17,74] gels. An increase in the stability of aluminium naphthenate gels (6%) (both pure and filled with aerosil) in medicinal liquid paraffin as a result of the superposition of harmonic oscillations at a constant rate of shear has been demonstrated[169,189]. It has been noted[190] that the measurement of the dynamic moduli of soap gels itself causes some disruption of the structure. A considerable increase in the stability of hydrocarbon gels of ammonium abietate under the conditions of shear has been observed[191].

In discussing these instances of dilatancy, it is necessary to take into account the microheterogeneous nature of surfactant gels. Presumably, at sufficiently high rates of shear the elements of the gel lattice—floccules consisting of associated surfactant and solvent molecules (ions)—have insufficient time to relax and therefore decompose, which leads to constrained conditions and the formation of structures analogous to PCS_2. This explanation is consistent with the results of a number of studies. Thus a study[192] of the rheological properties of plastic calcium greases, consisting of soap–oil gels, established that (a) the size and shape of the particles of the disperse phase (soap fibres) have a decisive influence on the properties of the grease and (b) a decrease in the size of these particles is accomapnied by an increase of viscosity and stability and also by an increase of the colloidal stability of the system. The common features in the mechanism of the influences of the degree of dispersion, the distribution of grain sizes, and peptisation on the structural-mechanical properties of PCS of various types can be readily seen. Incidentally, calcium greases are optically anisotropic, which shows that the structure is ordered[193].

The results of the investigation of "filled" systems, which are of great theoretical and practical importance, have been published in a number of communications[169,170,189,190,194,195]. The phenomenon of the breakdown of the aluminium naphthenate gel structure in liquid paraffin filled with aerosil has been investigated[170] with periodic deformations and with stabilisation of the structure in unidirectional deformation. It has been established[194] that aqueous bentonite gels, to which a small amount (a fraction %) of non-ionic surfactants has been added, are thixotropic systems; in the presence of ionic surfactants (anionic or cationic) these gels exhibit dilatant properties. It is significant that surfactants, or more correctly the DIL arising on the surface of adsorption layers, are responsible for the change in the properties of bentonite gels¶. On the other hand, the clay particles themselves, being "encapsulated", play an auxiliary role in this process. Such systems can be regarded as intermediate between typical hydrophobic dispersions and micellar solutions. On the other hand, it has been shown[196] that low-tar bitumens with a high content of asphaltenes behave like typical disperse systems, while high-tar bitumens with a low content of asphaltenes have rheological properties similar to those of concentrated polymer solutions. Bitumens with transitional properties are located between these extreme structural-rheological types.

(b) Dilatational Surface Viscosity of Monolayers

A method has been proposed[197] for the determination of the surface viscosities of surfactant monolayers based on the joint dynamic study of the surface pressure and the surface potential; the results of the investigation of the dynamic properties of insoluble elastic and highly elastic monolayers, which permit the determination of the role of the dilatational viscosity in the behaviour of these monolayers, have been published. The behaviour of a liquid drop in another liquid phase has been analysed[198]; it was shown that the period of circulation in the equatorial plane of the drop can be used to calculate the quantity $3k + 2\varepsilon$, where k is the dilatational surface viscosity and ε is the surface shear viscosity. A method for the determination of k has also been proposed in another study[199]†.

VI. DILATANCY OF SOLUTIONS OF HIGH-MOLECULAR-WEIGHT COMPOUNDS

Polymeric molecules frequently form aggregates or associated complexes in solution, such behaviour being usually quite pronounced in solutions of polar polymers and polyelectrolytes. As a result of the interaction of the aggregates, ordered structures may arise, which are analogous, on the one hand, to PCS, and, on the other hand, to liquid crystals[201–208]; this can be accounted for by the common features of the operation of ionic-electrostatic and molecular forces in disperse systems and in polyelectrolyte solutions[99].

¶ In contrast to this, the non-ionic hydroxyethylated octyl alcohol adsorbed on particles of phthalocyanine pigments sharply decreases the thixotropy of the dispersion as a consequence of the formation of fairly extensive ASL.[195]

†The dilatational viscoelastic properties of a thick film with a single soluble surfactant have been analysed quantitatively[200].

In a number of recent studies it has been shown that solutions of many polymers are structured. Thus the presence of involved ordered complexes—globular associated species and microgels (the authors[213] believe that these formations can be compared with colloidal particles)—has been demonstrated[209-212] in aqueous solutions of poly(vinyl alcohol) (PVA). It has been observed[214] by thermal, rheological, and morphological methods that very large aggregates of hydrated macromolecules exist in aqueous solutions of polyvinylpyrrolidinone, hydroxyethyl-starch, poly(vinyl alcohol), and poly(ethylene glycol). The aggregation of macromolecules in solutions of different polymers has also been discussed in a series of other studies[215-217]. Rheological studies of a solution of polyisobutylene in liquid paraffin have led to the conclusion[218] that structures made up of polymer chains exist in this solution.

Structured solutions of many polymers have dilatant (antithixotropic) properties[110,111,218-231]. Various factors determining the onset of the dilatant deformation regime have been described in the literature. Some investigators point to the orientation of the structural elements of the polymer, their aggregation and crystallisation, caused by the gradient flux, as well as mixing as fundamental factors in dilatancy[221, 232-237]. Ordered aggregates of macromolecules, strongly interacting with the solvent, constitute a kind of hydrates oriented in the flow[209-212,238-242]. Freshly formed gel fibres have an analogous structure[243]; the crystalline nature of fibrils containing the solvent has been noted[240,244-246]. It has been claimed in a number of studies that the principal condition for the occurrence of dilatancy is low solubility of the polymer and the consequent presence of associated complexes and aggregates of molecular chains (see Refs. 226, 230, 232, etc.). It has been shown[247] that the existence of a fluctuation network in solutions of methyl methacrylate–methacrylic acid copolymers is responsible for antithixotropy both under the conditions of simple shear and in complex (predominantly longitudinal) flow deformations.

The data presented permit the conclusion that the increased viscosity of polymer solutions under the conditions of shear is a consequence of the peptisation of the associated chain species and chain aggregates and of the appearance of constrained conditions, under which deaggregated formations—partly decomposed aggregates and individual macromolecules as well as their separate units—interact. When the degree of structure formation in the solution is low, complex and structure formation intensify in the first deformation stage[224]. At higher rates there is also a possibility of the peptisation of more stable complexes, leading to constrained conditions in dilatancy[138].

The ideas developed here are consistent with experimental data and with the conclusions of other investigators. Thus the formation of a second structure under the conditions of shear deformations after the partial breakdown of the first structure in polymer solutions has been discussed[218]. Evidently the second structure arises as a result of the peptisation of the first structure with formation of uniformly distributed solvated microfibrils under constrained conditions. The increase of viscosity in the initial state of the deformation of solutions of a number of polymers has been explained[248-250] by orientational effects. The observed relative expansion of fibrous polymer gels in the extension process has been attributed[248] to a rearrangement of their structure.

The peptisation of aggregates and microgel particles in polymer solutions can be illustrated by an example from the technology of paper manufacture. The grinding of a freely flowing paper mass by a roller reduces mainly to the dispersion of large fibrous particles until very fine hydrated fibres (fibrils) are obtained. For a high degree of grinding (for "fat" or "slimy" grinding), the mass becomes gel-like with an increased viscosity, which is due to the increase of the overall surface area of the fibrils and the decrease of ϕ_v.[251] In this case the freely disperse system is converted into PCS_2 as a result of peptisation. To complete the analogy, one can imagine that after fat grinding the fibrilled mass undergoes further dispersion up to "molecular" peptisation with formation of a "structured solution" possessing dilatant properties and resembling the usual dilatant polymer solutions[5].

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The common features in the rheological behaviour of PCS and polymer solutions, determined by the following common characteristics of the interaction of micro-objects, may be noted.

1. PCS_2 are dilatant as a consequence of the dominant operation of repulsion forces in the system, or, in other words, the manifestation of the positive disjoining pressure $\Pi_2 > 0$; PCS_1 are thixotropic and are characterised by a negative disjoining pressure $\Pi_1 < 0$.

2. In polymer solutions the peptisation or deaggregation of structural elements (complexes, associated species) under conditions involving the stabilisation of the ASL or DIL deaggregation products leads to a decrease of ϕ_v, a more uniform distribution of the polymer, and constrained conditions. This is possible when the polymer particles are adequately solvated or protected by ionic layers and the repulsion forces predominate, i.e. $\Pi_2^1 > 0$, which is responsible for dilatancy. If the deaggregation products in solution are not resistant to mutual adhesion, i.e. $\Pi_1^1 < 0$, then in the breakdown process the deformation of structures of one kind will be accompanied by the appearance of those of another, denser kind; the "network continuity" will then be infringed and the viscosity will correspondingly diminish.

The phenomenon of dilatancy has been considered in this review in the simplest form where the increase of the resistance to shear is determined mainly by the properties of the liquid layers separating the micro-objects. However, it is frequently complicated by various concomitant aggregation processes of different kinds, which have been enumerated in the second section. Furthermore, regardless of external influences, syneresis takes place spontaneously in disperse systems, while various processes involving the deaggregation of dissolved polymers, which may be intensified on deformation, occur in solutions of high-molecular-weight compounds[218, 252-254]. As a result of this, the processes occurring in the flow can be of a complex type whose determination is the next primary task of rheology. In particular, in view of the large particle size (of sand or other substances) and close packing, which hinders the movement of the particles during shear, classical dilatancy is a limiting if not an exceptional case. Here too the operation of common factors (ASL and DIL) is manifested, but under conditions of major constraint determined by the low value of ϕ_v (or by the ratio of the volume concentration of the disperse phase to the maximum attainable close packing, approaching unity[56]).

Consideration of the mechanism of the dilatancy of colloidal structures raises the question of the invariance of the rheological characteristics of non-Newtonian liquids. It is found that the flow parameters, determining the onset of the dilatant flow regime, depend on the deformation conditions[146,179]. Bearing this factor in mind, Strivens[146] notes that the dilatant effect observed on deformation is a kind of instrumental artifact. Further study of the energetic and kinetic aspects of the interaction of micro-objects will make it possible to establish the relation between the microparameters of the dispersion and its integral characteristics, which constitutes the basis of the development of methods for the

rational regulation of the structural-mechanical properties of dispersions and will also permit the construction of a quantitative theory of dilatant-thixotropic transformations in colloidal structures.

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Advances and Prospects in the Chemistry of Nucleoaminoacids and Nucleopeptides

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The present state of research into the development of methods of synthesis and into properties of aminoacids containing a natural nucleic acid base in the side chain (nucleoaminoacids) as well as the peptides formed from nucleoaminoacids (nucleopeptides) is examined. Attention is concentrated on the description of naturally-occurring representatives of these classes of compounds and on the analysis of prospects for their further investigation and use.
The bibliography includes 64 references.

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I. INTRODUCTION

Pyrimidine and purine bases are widely distributed in nature and play an important role in vital processes. They are obligatory structural components of all nucleic acids without exception. Many coenzymes, vitamins, and antibiotics are purine- or pyrimidine derivatives; the pyrimidine ring is the basis of many most important natural condensed systems (pteridines, isoalloxazines, etc.). α-Aminoacids, which constitute the elementary structural units of peptides and proteins and occupy one of the central positions among known natural products, are no less important and are just as widely distributed in biological systems.

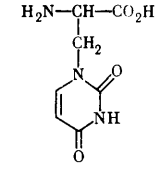
One may claim that pyrimidine and purine derivatives as well as α-aminoacids belong to chemical structures which permeate the entire spectrum of life, starting from viruses and extending to higher animals and man.

The chemical research into the above heterocyclic compounds, on the one side, and α-aminoacids and peptides, on the other, was prosecuted for a long time in isolation and such investigations did not as a rule overlap. Nevertheless, biochemical and molecular biological data undoubtedly indicate the occurrence in biological systems of very intimate interactions, combining these classes of natural products. This has been manifested not only in the study of metabolic pathways involving these structures but also in the detection in nature of various aminoacids (and recently also peptides) derived from pyrimidine and purines.

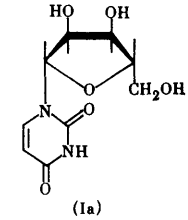
Among the wide variety of pyrimidinyl- and purinyl-aminoacids, *nucleoaminoacids* are of special interest[1]. Here and henceforth this term will be used to designate α-amino-carboxylic acids with pyrimidine or purine nucleic acid bases in the side chain, attached to the aminoacid fragment via the N^1 (pyrimidine) or N^9 (purine) atom.

In conformity with the above definition, the structure of nucleoaminoacids follows unambiguously from the structures of the known nucleic acid bases. If we disregard for the moment the minor nucleic acid bases and confine ourselves to the principal nucleic acid bases (uracil, thymine, cytosine, adenine, and guanine) and if among all the aminoacid fragments only the α-alanine fragment is considered, then typical examples of the class of nucleoaminoacids are β-(N^1-uracilyl)-α-alanine (I), β-(N^1-thyminyl)-α-alanine (II), β-(N^1-cytosinyl)-α-alanine (III), β-(N^9-adeninyl)-α-alanine (IV), and β-(N^9-guaninyl)-α-alanine (V). The three-letter abbreviations for these nucleoaminoacid residues are Ual, Tal, Cal, Aal, and Gal respectively.

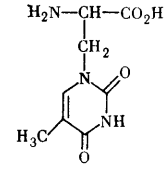
Comparison of the structure of nucleoaminoacids with that of the corresponding nucleosides of the pyrimidine and purine series shows readily that nucleoaminoacids are aminoacid analogues of the natural nucleosides (Ia)–(Va), differing from the latter by the substitution of the pentose (ribose or deoxyribose) residue by the aminoacid fragment:



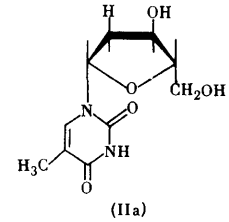
(I)



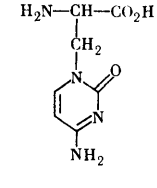
(Ia)



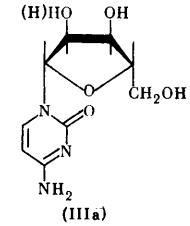
(II)



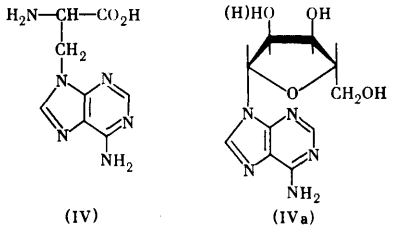
(IIa)



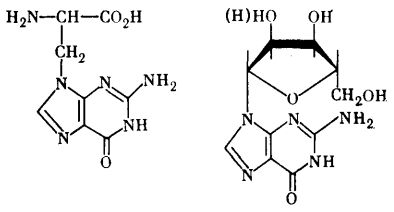
(III)



(IIIa)



(IV) (IVa)

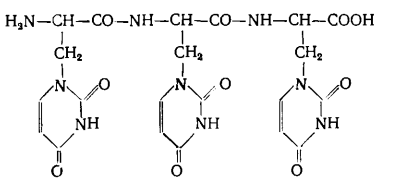


(V) (Va)

When nucleoaminoacid residues are linked together by peptide bonds, *nucleopeptides* are formed[1]. Here and henceforth this term will be used to designate peptides containing nucleoaminoacid residues. Whereas nucleic acid bases in oligonucleotides are attached to the pentose phosphate skeleton, in nucleopeptides the bases form a framework around the peptide chain.

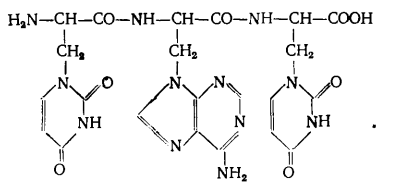
Depending on the qualitative composition, nucleopeptides can in general be divided into three main types: (1) homonucleopeptides; (2) heteronucleopeptides; (3) mixonucleopeptides.

Homonucleopeptides. These are nucleopeptides made up of repeating units of the same nucleoaminoacid. The tripeptide (VI), made up exclusively of β-(N^1-uracilyl)-α-alanine residues, is an example of a homonucleopeptide (the structure of this tripeptide is formulated in an abbreviated form in brackets underneath the formula below):



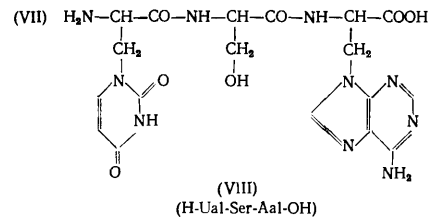
(VI) (H-Ual-Ual-Ual-OH)

Heteronucleopeptides. These are nucleopeptides made up of different nucleoaminoacid residues. The tripeptide (VII), whose composition includes two β-(N^1-uracilyl)-α-alanine residues and one β-(N^9-adeninyl)-α-alanine residue, is a typical example of heteronucleopeptides:



(VII)
(H-Ual-Aal-Ual-OH)

Mixonucleopeptides (synonym—nucleopeptides of the mixed type). These are peptides containing, together with nucleoaminoacid residues, also the residues of other aminoacids (in particular protein aminoacids). The tripeptide (VIII), whose composition includes the residues of β-(N^1-uracilyl)-α-alanine, serine (a protein aminoacid), and β-(N^9-adeninyl)-α-alanine, may serve as an example of a mixonucleopeptide:



(VIII)
(H-Ual-Ser-Aal-OH)

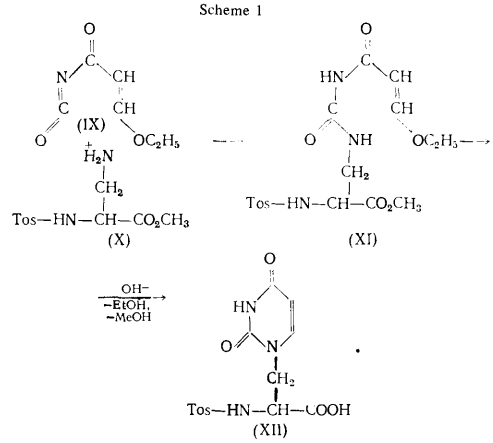
The methods of synthesis and the reactions of nucleoaminoacids are considered below, the methods of synthesis and properties of nucleopeptides are described, and the prospects for the further study and utilisation of nucleopeptides and nucleoaminoacids are discussed.

II. SYNTHESIS OF NUCLEOAMINOACIDS

All the methods of synthesis of nucleoaminoacids known at the present time can be divided by convention into two main groups: (1) methods of synthesis based on reactions in which the pyrimidine or purine ring is formed during the synthesis of the compound: (2) methods of synthesis in which a substituent is introduced into a complete hydropyrimidine or purine.

A typical example of the first group of methods of synthesis of nucleoaminoacids is the synthesis of the N^{α}-tosyl derivative of β-(N^1-uracilyl)-α-alanine [compound (XII)] by Kjaer et al.[2], which is based on the intramolecular cyclisation of the asymmetrically substituted urea (XI), formed on condensation of β-ethoxyacryloyl isocyanate (IX) with methyl α-tosylamino-β-DL-aminopropionate (X) via Scheme 1.

Scheme 1



(X) (XI) (XII)

It must be emphasised that initially the interest of investigators in the development of methods of synthesis of nucleoaminoacids was to a large extent stimulated by the detection of individual representatives of the class of nucleoaminoacids in nature. The first report of the possible presence of naturally-occurring nucleoaminoacids, by the German biochemist Gmelin[3], appeared at the end of 1959. In his study of extracts from the seeds of *Acacia willardiana*, Gmelin detected in them a new aminoacid, which he called "willardiine".

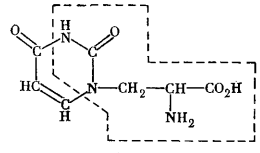
Subsequently Gmelin was able to isolate this aminoacid on a preparative scale and to show that its composition corresponds to the overall formula $C_7H_9N_3O_4.H_2O$. One of the remarkable properties of the new aminoacid was its capacity to absorb ultraviolet light intensely. The study of the ultraviolet absorption spectra of willardiine at different pH showed that they are extremely similar to the corresponding spectra in the near ultraviolet of compounds such as uridine and 1-methyluracil. Investigation of the infrared spectra of willardiine also revealed the presence of characteristic frequencies corresponding to the uracil ring; furthermore, it was concluded that the infrared spectra of willardiine contain absorption bands characteristic of the alanine fragment.

The hypothesis that willardiine may constitute a structure in which the alanine residue is linked to one of the oxygen atoms in the uracil molecule was abandoned when it was established[3] that the new aminoacid is extremely stable and, in particular, does not change on prolonged refluxing with 28% hydrobromic acid. If the alanine residue were linked to one of the oxygen atoms of the uracil molecule, then serine would have been inevitably formed under these conditions, which was not observed.

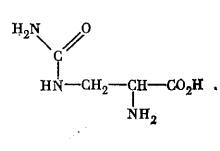
A more detailed study of the ultraviolet absorption spectra of willardiine[3] made it possible subsequently to eliminate from consideration variants of the structure which involved the addition of the alanine residue to the uracil ring via its carbon atoms in the 5- or 6-position and also via the nitrogen heteroatom in the 3-position. The last variant was rejected on the grounds that the ultraviolet spectra of willardiine, recorded at different pH, did not exhibit a bathochromic shift of λ_{max} with increasing alkalinity of the medium, which is known to be a characteristic property of 3-substituted uracils and is not observed in the spectra of 1-substituted uracils[4-6].

As a result of his investigations, Gmelin[3] concluded that willardiine apparently has a structure in which the alanine fragment is linked to the uracil ring and that the most probable point of addition of the alanine chain is the nitrogen heteroatom in the 1-position in the uracil ring. In other words, Gmelin suggested that the new natural aminoacid which he isolated has the structure of L-β-(N^1-uracilyl)-α-alanine (I).[3]

The fact that, long before the discovery of willardiine, a hitherto also unknown acyclic aminoacid was detected in plants of the family of Mimosaceae and was called "albizziine" [7,8] is noteworthy. It was subsequently shown unambiguously to have the structure of L-α-amino-β-ureidopropionic acid (XIII):[9,10]



(I)



(XIII)

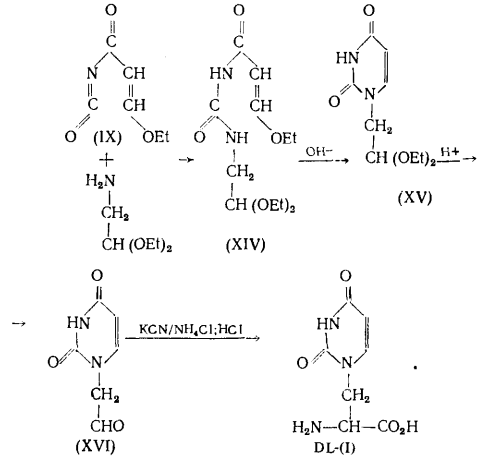
Gmelin was able to demonstrate that albizziine is present together with willardiine in the seeds of *Acacia willardiana*, *Acacia millefolia*, *Acacia lemmoni*, and *Mimosa asperata*.[3] This observation and the evident analogy between the molecular structures of (I) and (XIII) constituted additional arguments in support of structure (I) proposed for willardiine. Furthermore, on the basis of the above observation, Gmelin put forward the hypothesis that albizziine (XIII) can be a bioprecursor of willardiine[3].

All these ideas agree satisfactorily with one another and are consistent with a logical general scheme. However, one must not forget that at that time there was no final and rigorous proof that willardiine does indeed have structure (I). The question of the possible existence of nucleoaminoacids in nature therefore remained open.

The resulting situation was finally clarified when structure (I) of willardiine was demonstrated rigorously in 1961 by unambiguous chemical syntheses of this substance carried out almost simultaneously and independently by two groups of chemists—in Denmark[2] and in England[11,12].

The English investigators initially reported the synthesis of DL-β-(N^1-uracilyl)-α-alanine[11] from β-ethoxyacryloyl isocyanate (IX) which they had obtained previously[13,14]. Treatment of compound (IX) with the diethyl acetal of aminoacetaldehyde led to the formation of the disubstituted urea (XIV), which underwent intramolecular cyclisation on being heated in an aqueous solution of sodium hydroxide, accompanied by the elimination of an ethanol molecule and the formation of N^1-(2′,2′-diethoxyethyl)uracil (XV). Acid hydrolysis of the latter then yielded N^1-uracilylacetaldehyde (XVI), which was introduced into the cyanohydrin synthesis reaction, ensuring the unambiguous formation of DL-β-(N^1-uracilyl)-α-alanine via Scheme 2.

Scheme 2



As was to be expected, apart from the positive response to the ninhydrin test, the compound was able to absorb ultraviolet light intensely. Comparison of the ultraviolet spectra and other characteristics of the synthetic compound (I) and natural willardiine led to the conclusion that the chemical structures of these substances are identical.

Later the English investigators reported the separation of the racemic aminoacid (I) into its optical isomers[12]. For this purpose, the N^{α}-formyl derivative was obtained from the racemic aminoacid (I) and was treated with the dextrorotatory isomer of methylphenylaminomethane. The resulting mixture of diastereoisomeric salts was subjected to fractional crystallisation, which led to the isolation of the laevorotatory isomer of β-(N^1-uracilyl)-α-alanine, whose properties, including the magnitude and sign of the specific optical rotation, proved to be identical with those of natural willardiine[12].

Although these studies did not solve the problem of the absolute configuration of willardiine, they did not leave any doubt about the natural aminoacid being a nucleoaminoacid whose structure is identical with that of compound (I).

The fact that Dewar and Shaw[12] were unable to convert N^1-uracilyl-acetaldehyde (XVI) into compound (I) by the hydantoin method of synthesis[15,16] instead of the cyanohydrin method is noteworthy. This attempt led to the formation of the corresponding 1-hydantoinylmethyluracil; however, this compound proved to be extremely stable and did not hydrolyse even after prolonged heating at 150 °C with 10 *N* hydrochloric acid in a sealed tube[12].

Danish investigators[2] carried out an unambiguous synthesis of β-(N^1-uracilyl)-α-alanine (I) by the somewhat different procedure illustrated in Scheme 1 (see above). They obtained N^{α}-tosyl-DL-β-(N^1-uracilyl)-α-alanine (XII) in an analytically pure state. Further studies showed that this compound is chromatographically identical with the substance obtained on tosylation of natural willardiine[2]. This constituted independent proof that the new natural amino-acid has the structure of β-(N^1-uracilyl)-α-alanine.

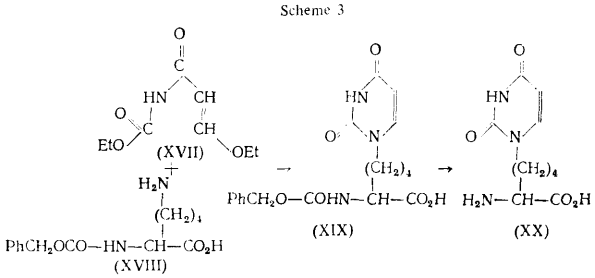
Kjaer et al.[2] studied the possibility of detosylating compound (XII) in order to obtain synthetic DL-β-(N^1-uracilyl)-α-alanine. However, they found that treatment of compound (XII) with sodium in liquid ammonia entails the breakdown of the uracil ring and the appearance of a whole "family" of aminoacids which did not absorb in the ultra-violet, one of which was identified as α,β-diaminopropionic acid. Treatment of the N^{α}-tosyl derivative of willardiine with a solution of hydrogen bromide in glacial acetic acid (for 3 h at 70 °C [17]) results in the complete removal of the protecting tosyl group; however, according to the above author's data[2], this involves extensive racemisation of the free aminoacid formed. When the duration of the detosylation process was reduced to 1 h, the Danish chemists were able to obtain from compound (XII) a substance whose infrared spectrum and specific optical rotation did not differ from those of natural willardiine. However, the yield of the optically active nucleoaminoacid (I) prepared in this way was extremely low (2%).

Thus the above method of preparing β-(N^1-uracilyl)-α-alanine, which solves in principle the problem of the complete chemical synthesis of this naturai nucleoaminoacid, does not permit its preparative synthesis in appreciable amounts.

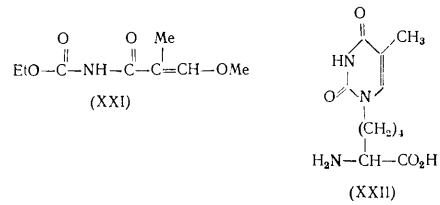
In this connection we should note that the method of synthesis of compound (I) proposed by the English investigators[12] also fails to solve the problem of the preparative synthesis of the nucleoaminoacid β-ethoxyacryloyl isocyanate, which they used as the starting material, is itself difficult to obtain[13,14]. Examination of the entire synthetic pathway leading to compound (IX) from ethyl bromoacetate shows that the yield of the diethyl acetal of N^1-uracilyl-acetaldehyde (XV), which is the key compound in this method of synthesis of β-(N^1-uracilyl)-α-alanine, is only 4% of theoretical.

In 1971 De Koning and Pandit[18] described the synthesis of α-amino-ε-(N^1-uracilyl)-caproic acid (XX) via Scheme 3, which provides for the condensation of 3-ethoxy-*N*-ethoxy-carbonylacrylamide (XVII) with N^{α}-benzyloxycarbonyl-lysine (XVIII). α-Amino-N^{α}-benzyloxycarbonyl-ε-(N^1-uracilyl)-caproic acid (XIX) is an intermediate in this synthesis.

Scheme 3

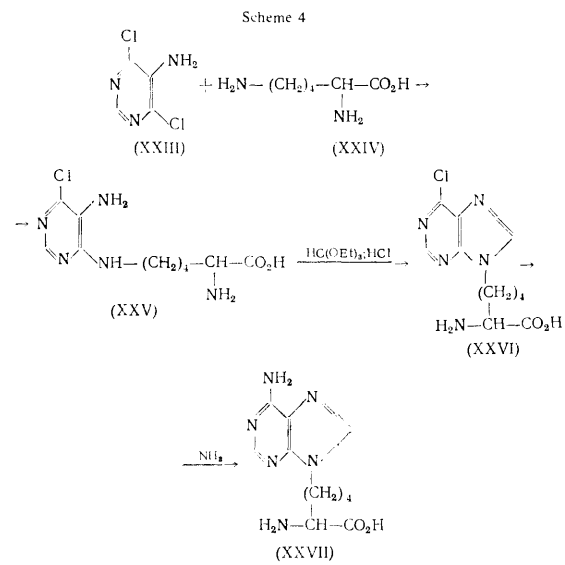


When *N*-ethoxycarbonyl-3-methoxy-2-methylacrylamide (XXI) was used in the condensation stage instead of compound (XVII), α-amino-ε-(N^1-thyminyl)-caproic acid (XXII) was obtained via an analogous scheme. The yield of the racemic nucleoaminoacids (XX) and (XXII) was approximately 40%.



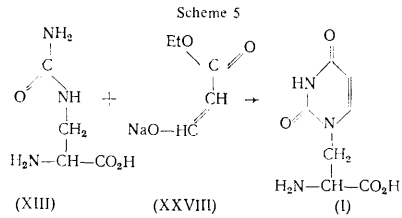
The first group of methods of synthesis also includes that of the synthesis of α-amino-ε-(6-chloro-N^9-purinyl)-caproic acid (XXVI). Compound (XXVI) is the key substance in the synthesis of ε-(N^9-adeninyl)-α-aminocaproic acid (XXVII).[19] A characteristic feature of the synthesis of compound (XXVI) is the formation of the purine ring as a result of the closure of the imidazole ring in the course of the synthesis via Scheme 4. The initial compounds are 5-amino-4,6-dichloro-pyrimidine (XXIII) and lysine (XXIV), while the pyrimidinyl-aminoacid (XXV) is an intermediate.

Scheme 4



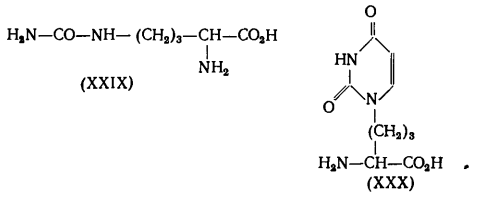
The method of synthesis of compound (I) by the condensation of α-amino-β-ureidopropionic acid (albizziine) with formylacetic ester also belongs to this group[20,21]. The ester is used in the form of the sodio-derivative (XXVIII) and condensation proceeds via Scheme 5.

Scheme 5



If citrulline (α-amino-δ-ureidovaleric acid (XXIX) is used in the analogous condensation instead of albizziine, then α-amino-δ-(N^1-uracilyl)valeric acid (XXX) can be

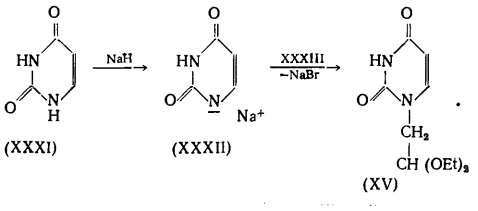
obtained[22]:



(XXIX) (XXX)

A new direct synthesis from uracil (XXXI) of compound (XV), i.e. N^1-(2′,2′-diethoxyethyl)uracil (the diethyl acetal of N^1-uracilylacetaldehyde), already mentioned above (see Scheme 2), was described in 1965.[23] According to these data[23], when compound (XXXI) is treated with sodium hydride in dimethylformamide, the sodio-derivative of uracil (XXXII) is formed initially and, on subsequent heating with 2-bromo-1,1-diethoxyethane (XXXIII), is smoothly converted into N^1-(2′,2′-diethoxyethyl)uracil (XV):

Scheme 6



(XXXI) (XXXII) (XV)

The yield of compound (XV), which is the key substance in the synthesis of nucleoaminoacids, is approximately 40%.

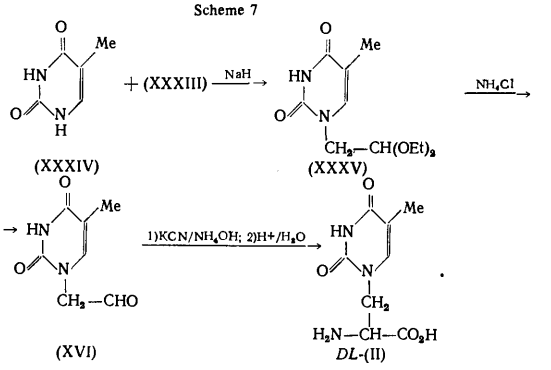
The formation of the N^1,N^3-disubstituted product (XXXV) takes place simultaneously (yield approximately 13%), but this substance can be separated comparatively readily from the desired compound (XV).

In contrast to Shaw and Dewar[11], who used acid hydrolysis, American investigators[23] suggested that the diethyl acetal of N^1-uracilyl-acetaldehyde be converted into free N^1-uracilyl-acetaldehyde by a milder process involving the heating of compound (XV) with an aqueous solution of ammonium chloride. Under these conditions, the yield of compound (XVI) was increased from 40 to 83%. The subsequent introduction of compound (XVI) into the cyanohydrin synthesis reaction makes it possible to obtain readily the racemic nucleoaminoacid (I) on a preparative scale by the scheme already described (Scheme 2).

The above method of synthesis of DL-β-(N^1-uracilyl)-α-alanine (I) was extended to other nucleoaminoacids. In particular, DL-β-(N^1-thyminyl)-α-alanine and DL-β-(N^1-cytosinyl)-α-alanine can be synthesised by this method[24,25].

The synthesis of DL-β-(N^1-thyminyl)-α-alanine is based on thymine (XXXIV) as the starting material and proceeds via the following scheme:

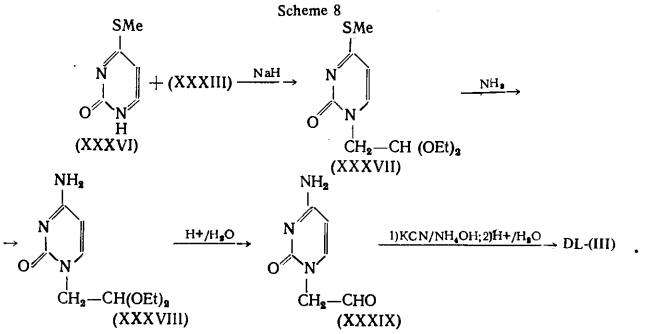
Scheme 7



(XXXIV) (XXXV) (XVI) DL-(II)

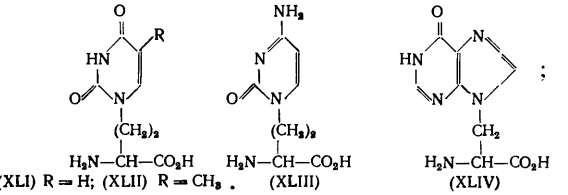
In the synthesis of DL-β-(N^1-cytosinyl)-α-alanine (III) the starting material is 4-methylthio-2-oxodihydropyrimidine (XXXVI):

Scheme 8



(XXXVI) (XXXVII) (XXXVIII) (XXXIX) DL-(III)

The interaction of uracil (XXXI), thymine (XXXIV), and 4-methylthio-2-oxodihydropyrimidine (XXXVI) with the diethyl acetal of γ-chloropropionaldehyde (XL) has also been investigated[25]. It was established that uracil and thymine give rise to both N^1- and N^3-derivatives, which can be readily separated by crystallisation. On the other hand, the exclusive formation of the N^1-isomer was noted in the case of 4-methylthio-2-oxodihydropyrimidine (XXXVI). These investigations led to the synthesis of α-amino-γ-(N^1-uracilyl)-butyric acid (XLI), α-amino-γ-(N^1-thyminyl)-butyric acid (XLII), and α-amino-γ-(N^1-cytosinyl)-butyric acid (XLIII):[25]



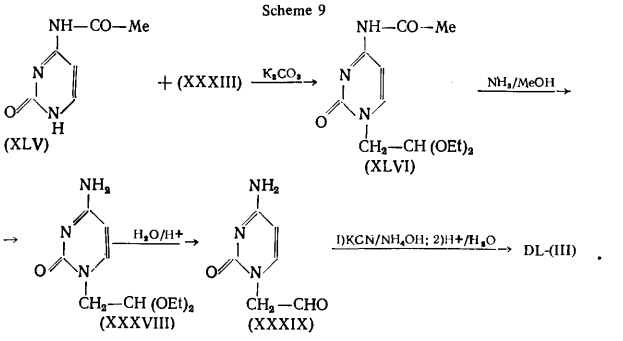
(XLI) R = H; (XLII) R = CH_3. (XLIII) (XLIV)

The reaction of heterocyclic bases with 2-bromo-1,1-diethoxyethane (XXXIII) was extended to the synthesis of a number of aminoacids of the purine series, including β-(N^9-adeninyl)-α-alanine and β-(N^9-hypoxanthinyl)-α-alanine (XLIV).[26,27] A series of β-(amino-N^9-purinyl)-α-alanines, including β-(N^9-guaninyl)-α-alanine, were synthesised with the aid of this reaction[28].

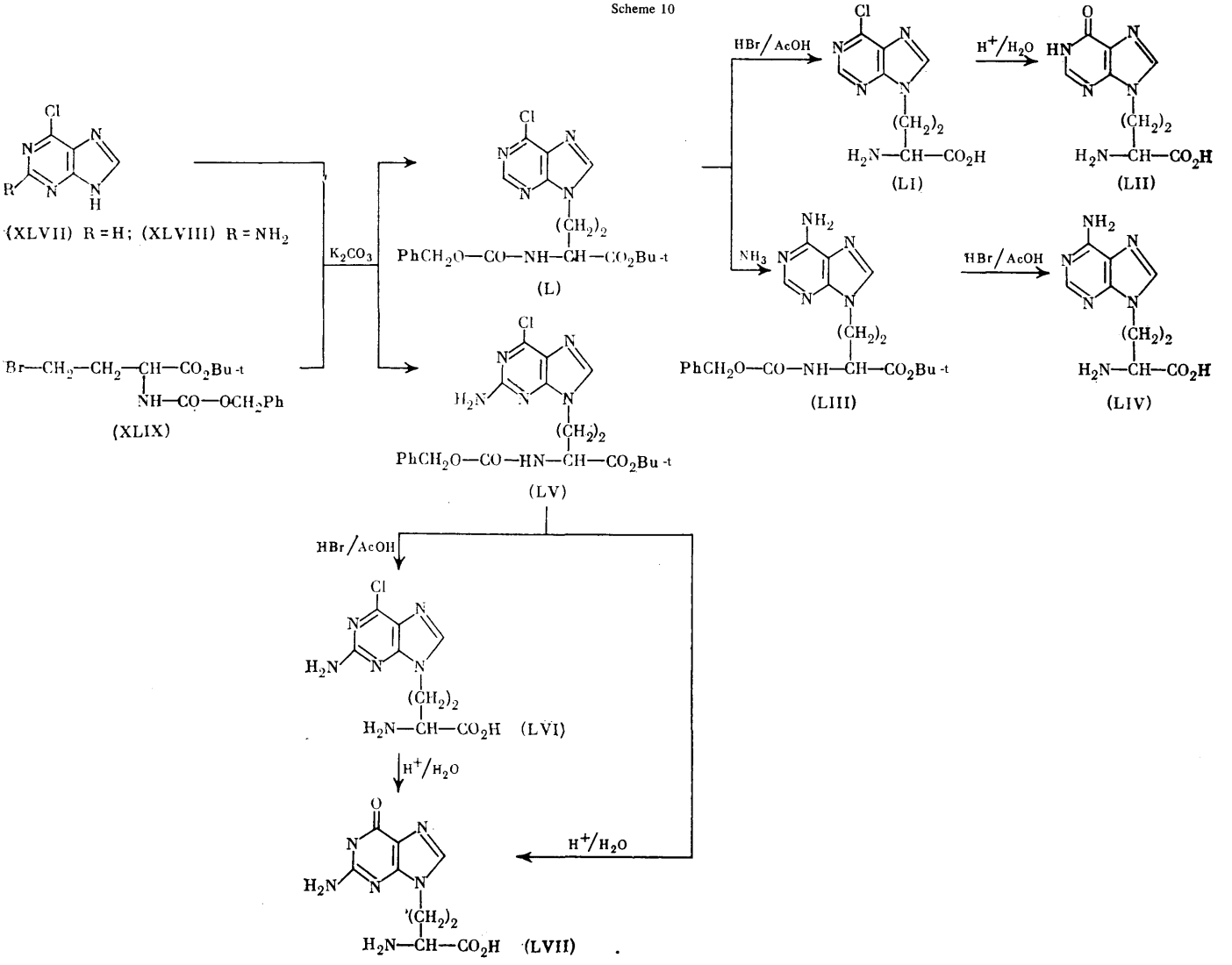
A further improvement of the method of synthesis of nucleoaminoacids based on the reaction of acetals of halogenoaldehydes with heterocyclic bases of the pyrimidine and purine series involved the use of potassium carbonate, proposed by Doel et al.[29], instead of sodium hydride in the alkylation stage. This change significantly simplified the method of synthesis, and, what is particularly important, made it possible to increase the yield of nucleoaminoacids to 50–60%.

Various nucleoaminoacids, including β-(N^1-thyminyl)-α-alanine and β-(N^9-adeninyl)-α-alanine, were synthesised by this modified method. In the synthesis of β-(N^1-cytosinyl)-α-alanine by this procedure, the starting material can be 4-*N*-acetylcytosine (XLV) and the intermediates in this instance are the diethyl acetal of 4-*N*-acetyl-N^1-cytosinylacetaldehyde (XLVI), the diethyl acetal of N^1-cytosinylacetaldehyde (XXXVIII) and, directly, N^1-cytosinylacetaldehyde (XXXIX):

Scheme 9



Scheme 10



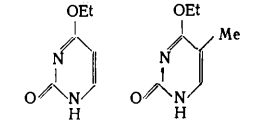
This method is most frequently used nowadays for the synthesis of various nucleoaminoacids, particularly nucleoalanines.

A variant of this method is the synthesis of nucleoaminoacids by the alkylation of pyrimidine or purine bases with the corresponding halogeno-derivatives of protected aliphatic aminoacids. For example, Nollet et al.[30] described the synthesis of a series of nucleoaminoacids of the purine series via Scheme 10, which provides for the use of various 6-chloropurines and potassium carbonate as the starting materials and of t-butyl γ-benzyloxycarbonylamino-α-bromobutyric acid (XLIX) as the alkylating agent. α-Amino-γ-(N^9-hypoxanthinyl)-butyric acid (LII), γ-(N^9-adeninyl)-α-aminobutyric acid (LIV), and α-amino-γ-(N^9-guaninyl)butyric acid (LVII) have been synthesised using this compound[30].

The alkylation reactions proceed with high yields (70 to 88%) in these syntheses and lead to the preferential formation of the N^9-derivatives. Admixtures of the isomeric N^7-derivatives did not exceed 10–11% in all cases and could be readily separated by chromatography on alumina.

Nollet and Pandit[31] also described the synthesis via an analogous scheme of α-amino-γ-(N^1-uracilyl)butyric acid (XLI), α-amino-γ-(N^1-cytosinyl)butyric acid (XLIII), and α-amino-γ-(N^1-thyminyl)butyric acid (XLII).

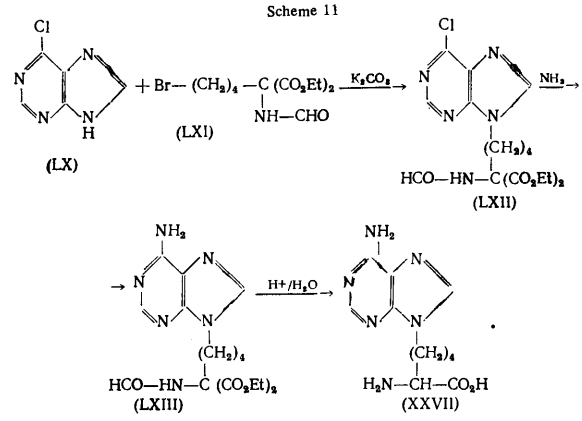
The nucleoaminoacids (XLI) and (XLII) were synthesised from 4-ethoxy-2-oxodihydropyrimidine (LVIII); on the other hand, in the synthesis of the nucleoaminoacid (XLII) the starting material was 4-ethoxy-5-methyl-2-oxodihydropyrimidine (LIX). The alkylation stages in these syntheses were carried out using sodium hydride.



(LVIII) (LIX)

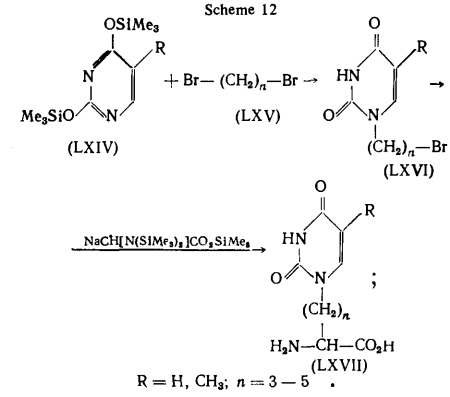
De Koning and Pandit[18] also used halogenoacylaminomalonic esters for the alkylation of heterocyclic bases. In particular, they obtained α-(4-bromobutyl)-α-formylaminomalonic ester (LXI) by the reaction of 1,4-dibromobutane with formylaminomalonic ester and then used it as the alkylating agent in the synthesis of ε-(N^9-adeninyl)-α-aminocaproic acid via the following scheme:

Scheme 11



Another sequence of reactions ensuring the formation of nucleoaminoacids by the alkylation of complete heterocyclic structures has been proposed[32].

Scheme 12

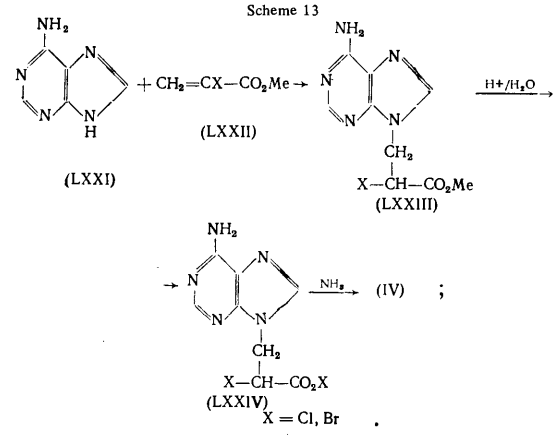


The principle of the method is that the heterocyclic structure is initially treated with an α,ω-dihalogenoalkane and the resulting ω-halogenoalkyl derivative of the pyrimidine or purine series is then converted into the corresponding nucleoaminoacid. The specific stages of this method are indicated in Scheme 12. α-Amino-ε-(N^1-uracilyl)caproic acid (XX) and α-amino-ε-(N^1-thyminyl)caproic acid (XXII), as well as the previously unknown α-amino-δ-(N^1-thyminyl)-valeric acid (LXVIII), α-amino-ω-(N^1-uracilyl)oenanthic acid (LXIX), and α-amino-ω-(N^1-thyminyl)oenanthic acid (LXX) have been synthesised by this method.

Japanese investigators[33] recently reported the synthesis via the alkylation reactions of a special group of nucleoaminoacids in which the pyrimidine or purine ring is linked directly to the α-carbon atom of the aminoacid residue.

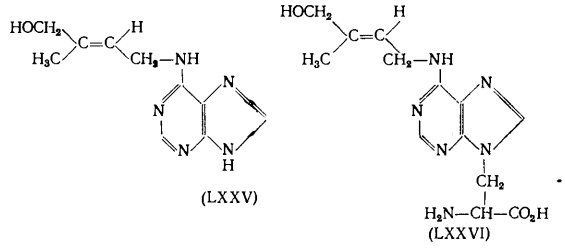
Instead of the alkylation of heterocyclic derivatives, one can use in the synthesis of nucleoaminoacids the reaction involving the addition of the corresponding nucleic acid bases to unsaturated compounds with an activated double bond. The preparation of β-(N^9-adeninyl)-α-alanine via Scheme 13, in which adenine (LXXI) and methyl α-halogenoacrylate (LXXII) are used as the starting materials[34], can serve as an example of such synthesis:

Scheme 13



The methyl ester of the corresponding β-(N^9-adeninyl)-α-halogenopropionic acid (LXXIII) and free β-(N^9-adeninyl)-α-halogenopropionic acid (LXXIV) are intermediates in this synthesis. The addition of adenine to methyl α-halogenoacrylate takes place with 80–85% yield, which ensures a fairly high overall yield of the nucleoaminoacid.

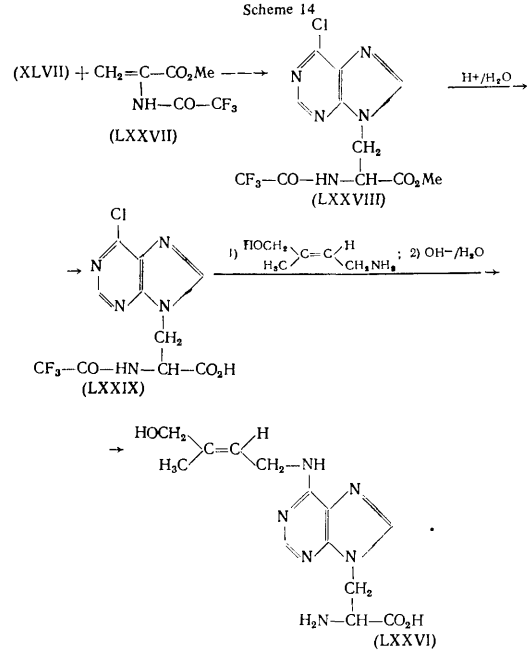
An analogous scheme can be used successfully also in the synthesis of other nucleoaminoacids of the purine series. Thus the method has been employed[35] to synthesise lupinic acid (LXXVI), which is a natural purine nucleoaminoacid. Lupinic acid was first isolated by Australian investigators[35,36] from prickly lupin (*Lupinus angustifolius*) and can be regarded as the N^9-alanine derivative of the familiar phytohormone zeatin (LXXV):



(LXXV) (LXXVI)

Lupinic acid can be regarded just as reasonably as a derivative of the nucleoaminoacid (IV) with the substituent in the exocyclic 6-aminogroup. Racemic lupinic acid has been synthesised via the following scheme[35]:

Scheme 14



The overall yield of compound (LXXVI) was approximately 5% (relative to the initial 6-chloropurine).

III. PROPERTIES OF NUCLEOAMINOACIDS

All the nucleoaminoacids known at present are colourless crystalline substances in a free state with high melting points. The solubilities of nucleoaminoacids in water are various and depend both on the nature of the nucleic acid base and on the length of the hydrocarbon chain linking the nucleic acid base to the α-carbon atom of the nucleoaminoacid. Nucleoaminoacids are almost insoluble in non-polar organic solvents. As typical amphoteric compounds, nucleoaminoacids are as a rule readily soluble in acid and alkaline aqueous solutions.

The ultraviolet spectroscopy occupies a special place in the study of the structures and physical properties of nucleoaminoacids (both naturally-occurring and synthetic). In many instances this technique makes it possible to solve convincingly and unambiguously the important problem of the cycloaddition of the aminoacid fragment to the nucleic acid base. Thus in the case of substituted uracils and analogous compounds of the pyrimidine series the large bathochromic shift of λ_{max} in the ultraviolet spectra of alkaline solutions of the test substances is characteristic of N^3-substituted derivatives. On the other hand, there is virtually no bathochromic shift in the spectra of the isomeric N^1-substituted derivatives in alkaline media[4-6,22].

NMR,[37,38] infrared spectroscopy[2,12,39], and mass spectrometry[35,36] are also useful in the solution of structural problems in the chemistry of nucleoaminoacids.

All the nucleoaminoacids give a positive response to tests with ninhydrin and other reagents forming characteristic coloured products on interaction with α-aminoacids. The chemical reactions of nucleoaminoacids can be divided into those involving the α-amino-group, the α-carboxy-group, and the nucleic acid base. The reactions of the first two types have now been particularly widely investigated. Methods of synthesis of N^{α}-protected nucleoaminoacids, in particular N^{α}-benzyloxycarbonyl-[40,41] and N^{α}-t-butoxycarbonyl-nucleoaminoacids[42-44] as well as nucleoaminoacid esters (including methyl, ethyl, and t-butyl esters[30,31,43,45]), amides[46], and hydrazides[45] have been developed on the basis of these studies. The synthesis of various activated esters of N^{α}-protected nucleoaminoacids (in particular, *p*-nitrophenyl, pentachlorophenyl, pentafluorophenyl, *N*-hydroxysuccinimido, and other esters) has also been achieved[45-47].

Takemoto et al.[48] obtained in a high yield and characterised the *N*-carboxyanhydride of β-(N^1-uracilyl)-α-alanine. The formyl[12], tosyl[2], *o*-nitrobenzenesulphenyl[44], 2,4-dinitrophenyl[45], and acetyl[49] derivatives of nucleoaminoacids have also been described in the literature.

The bromination and chlorination of certain nucleoaminoacids of the pyrimidine series in the 5-position in the pyrimidine ring by bromine and *N*-chlorosuccinimide respectively have also been studied[24].

Microbiological transformations as well as the chemical nature of the resulting products have been studied for certain nucleoaminoacids[52]. In particular, it has been established that a strain of *Microbacterium sp.* can utilise only the L-forms of compounds (I) and (II) as well as certain other nucleoaminoacids. This involves in the first place the oxidative deamination of the nucleoaminoacids and then the cleavage of the bond between the nitrogen atom in the 1-position in the pyrimidine ring and the β-carbon atom of the alanine fragment. Uracil, thymine, as well as the corresponding α-ketoacids of the pyrimidine series, which are apparently the precursors of the free nucleic acid bases formed, have been found among the microbiological transformation products of nucleoaminoacids.

IV. SYNTHESIS OF NUCLEOPEPTIDES

The reactions of peptide synthesis in solution, the methods of synthesis of peptides on insoluble polymeric carriers, as well as polycondensation reactions of carboxyl-activated derivatives of nucleoaminoacids can be used to synthesise nucleopeptides.

The synthesis of nucleopeptides in solution requires the preliminary solution of many special problems due to the

specific features of the chemical structures of nucleoaminoacids. The direct transfer to the synthesis of nucleopeptides of the traditional methods of the usual peptide synthesis, disregarding the characteristic features of the structure and reactivity of nucleoaminoacids, is in most cases relatively ineffective. At the same time there is much in common between the synthesis of nucleopeptides in solution and the usual peptide synthesis. In particular, as in the synthesis of normal peptides, made up of protein aminoacid residues, in the synthesis of nucleopeptides one must have at one's disposal the corresponding protected and activated derivatives of nucleoaminoacids, as well as reliable methods for the formation of peptide bonds between individual nucleoaminoacid residues.

The benzyloxycarbonyl and t-butoxycarbonyl groups are most often used in the synthesis of nucleopeptides in solution for the temporary protection of the α-aminogroup. In order to protect the carboxy-group, the nucleoaminoacids are first converted into esters (the methyl and ethyl esters are most often employed).

The carboxyl of the *N*-protected nucleoaminoacid used as the carboxy-component in nucleopeptide synthesis can be activated by the mixed anhydride or activated ester method as well as the azide and carbodi-imide methods.

Using the above protecting groups and methods of activation, a series of nucleopeptides incorporating the β-(N^1-uracilyl)-α-alanine residue have been synthesised[40,41]. The simplest representative of the family of homonucleopeptides—β-(N^1-uracilyl)-α-alanyl-β-(N^1-uracilyl)-α-alanine (LXXX)—was also obtained for the first time by this procedure. The syntheses of a series of oligonucleopeptides containing the α-amino-ε-(N^1-uracilyl)caproic acid (XX) and α-amino-ε-(N^1-thyminyl)caproic acid (XXII) residues[50], as well as other nucleoaminoacid residues of the pyrimidine and purine series[43,44,53,54] have been achieved analogously.

An example of the synthesis of nucleopeptides using insoluble polymeric carriers is provided by the synthesis of an oligonucleopeptide containing a monotonic block comprising nine repeating residues of compound (I).[55] The chloromethylated styrene–1% divinylbenzene copolymer was used as the insoluble carrier and the condensing agent was *N*,*N*′-dicyclohexylcarbodi-imide.

The nucleopeptide was separated from the polymeric carrier by hydrazinolysis. An oligonucleopeptide containing a monotonic block of repeating residues of compound (IV) has been synthesised via a similar scheme[56].

It is noteworthy that the synthesis of nucleopeptides on insoluble polymeric carriers involves many difficulties characteristic of the solid-phase synthesis of the usual peptides made up of protein α-aminoacid residues[57,58].

The polycondensation reactions of carboxyl-activated derivatives of nucleoaminoacids can be used to synthesise both homo- and hetero-nucleopeptides.

Homonucleopeptides containing the residues of nucleoaminoacids (I) or (II) have been synthesised by the polycondensation of the *p*-nitrophenyl esters of the nucleoaminoacids[59]. The molecular weight of the homonucleopeptides obtained is approximately 2000 according to sedimentation analysis and gel filtration data. Homonucleopeptides containing repeating units of nucleoaminoacids (XXII) or (XXVII) have been synthesised analogously[50]. Their yields were 85–90% and the molecular weight of the homonucleotide made up repeating nucleoaminoacid (XX) residues reached 5%.

Together with the polycondensation of *p*-nitrophenyl esters of nucleoaminoacids, the analogous reaction using the pentachlorophenyl esters of nucleoaminoacids has also been studied[46]. Compared with the *p*-nitrophenyl esters, the pentachlorophenyl esters of nucleoaminoacids are more reactive and make it possible to obtain longer homonucleopeptide chains.

Takemoto et al.[48] reported the synthesis of homonucleopeptides containing repeating residues of β-(N^1-uracilyl)-α-alanine from the *N*-carboxyanhydride of the same nucleoaminoacid. Aliphatic amines (in particular, mono-, di-, and tributylamines) were used as the initiators of the polycondensation reaction[48]. The same workers also reported the synthesis of mixonucleopeptides containing the residues of β-(N^1-uracilyl)-α-alanine and γ-benzylglutamic acid[48].

An important new stage in the study of nucleopeptides has been the development of methods of synthesis of hitherto unknown stereoregular nucleopeptides made up of optically pure, and not racemic, enantiomeric nucleoaminoacids. A necessary condition for the synthesis of stereoregular nucleopeptides was the development of preparative methods of synthesising the optical isomers of nucleoaminoacids.

The first attempts to obtain L-β-(N^1-uracilyl)-α-alanine were made by Kjaer and Knudsen[2] and Dewar ahd Shaw[12]. Kjaer and Knudsen[2] started with the optically active derivative of α,β-diaminopropionic acid. However, as already mentioned above, the difficulties arising in the stage involving the removal of the N^{α}-protecting groups prevented these investigators from obtaining L-β-(N^1-uracilyl)-α-alanine in preparative amounts. Dewar and Shaw[12] attempted to separate racemic β-(N^1-uracilyl)-α-alanine into optical isomers by forming diastereoisomeric salts with optically active bases. The latter consisted of the dextrorotatory enantiomer of α-methylphenylamine and natural laevorotatory brucine. However, these attempts were also unsuccessful as regards the preparative scale of the synthesis of optical isomers of nucleoaminoacids.

It was not until 1975–1976 that preparative methods for the synthesis of nucleoaminoacid enantiomers were developed. A special series of studies established that nucleoaminoacid racemates can be separated into optical isomers with the aid of the stereoselective enzymatic hydrolysis of the N^{α}-acyl derivatives of D,L-nucleoaminoacids by pig kidney acylase (I) [49] or plant acylase[51]. The possibility of using chymotrypsin for the stereoselective hydrolysis of racemic nucleoaminoacid esters was also demonstrated.

The use of the above methods made it possible for the first time to obtain the optical isomers of various nucleoaminoacids on a preparative scale. Using individual enantiomers of nucleoaminoacids, methods were then developed for the synthesis of protected and carboxyl-activated derivatives of optically active nucleoaminoacids, which led to the possibility of synthesising also stereoregular nucleopeptides. For example, the corresponding N^{α}-t-butoxycarbonyl derivatives and pentachlorophenyl esters have been synthesised from the L- and D-isomers of the nucleoaminoacid (I). They were made to undergo the polycondensation reaction, which yielded stereoisomeric homonucleotides made up of repeating L- (I) or D- (I) residues[60].

Various stereoisomeric mixonucleopeptides—in particular water-soluble stereoregular nucleopeptides of the mixed type made up of regularly alternating residues of compound L- (I)—have also been synthesised by an analogous procedure[61].

An important recent discovery has been the detection of naturally-occurring nucleopeptides of a mixed type. The isolation of two new willardiine peptides from the seeds of *Fagus silvaticus* has been reported[62,63]. The structures of γ-L-glutamyl-L-β-(N^1-uracilyl)-α-alanine (LXXXI) and γ-glutamylphenylalanyl-β-(N^1-uracilyl)-α-alanine (LXXXII) respectively have been proposed for the above peptides on the basis of a study of their chemical and spectroscopic

properties[62]. In view of the very limited amount of the second compound, the authors were unable to determine the stereochemical configuration of the aminoacid residues in this nucleotripeptide. The question of the synthesis of these new natural products also remained open.

Both problems were subsequently solved. Firstly, the total synthesis of the nucleopeptide (LXXXI) was carried out[64]. Secondly, authentic γ-L-glutamyl-L-phenylalanyl-L-β-(N^1-uracilyl)-α-alanine was synthesised. The natural nucleopeptides proved to be identical with the synthetic specimens[64]. Thus it can be regarded as proved that all three aminoacid residues in the nucleotripeptide (LXXXII) have the L-configuration.

V. PROPERTIES OF NUCLEOPEPTIDES

In a free state nucleopeptides are colourless crystalline or amorphous substances with high and as a rule non-characteristic melting points. The solubility of nucleopeptides in water varies within wide limits and depends on the nature of the aminoacid residues and on the length of the nucleopeptide chain. There is an overall tendency towards a decrease of the solubility of nucleopeptides in water with increase of the length of the nucleopeptide chains. Free nucleopeptides are almost insoluble in non-polar salts. Comparatively short nucleopeptides dissolve satisfactorily in aqueous solutions of acids and alkalies. The solubility of nucleopeptides of the mixed type can be regulated within wide limits by introducing "solubilising inserts" into the nucleopeptide chain. Thus water-soluble nucleopeptides of a mixed type can be obtained by introducing the residues of hydrophilic α-aminoacids (in particular serine, lysine, glutamic acid, etc.) into the nucleopeptide chain. The properties of long nucleopeptide chains have so far been inadequately investigated.

Short nucleopeptides can be used to prepare longer nucleopeptide chains either by the stepwise growing of the chain or by employing fragment polycondensation methods. At the same time short nucleopeptides are not only important intermediates but are also of independent interest, because these compounds can exhibit certain general properties characteristic of nucleopeptide structures.

One of these general properties is the interaction of the side groups in nucleopeptides. In nucleopeptides made up exclusively of nucleoaminoacid residues there is a possibility of observing the interaction between the corresponding nucleic acid bases. On the other hand, in nucleopeptides of the mixed type, incorporating various protein and non-proteinogenic aminoacid residues, together with those of nucleoaminoacids, the interaction of the nucleic acid bases with the side chains of aromatic and heterocyclic aminoacids merits attention.

Comparative study of the ultraviolet and ^{1}H NMR spectra of aqueous solutions of oligonucleopeptides incorporating the residues of nucleoaminoacid (I) as well as the residues of this nucleoaminoacid and phenylalanine showed[38] that secondary structures, stabilised by intramolecular hydrophobic stacking interactions, are formed in such nucleopeptides.

VI. PROSPECTS FOR THE STUDY OF NUCLEOAMINOACIDS AND NUCLEOPEPTIDES

The synthesis and investigation of nucleoaminoacids and nucleopeptides are of undoubted interest. Nucleoaminoacids are necessary for the synthesis of nucleopeptides. The latter can have unique properties, the unusual nature of which is determined by the combination, within the framework of a single molecule, of the peptide skeleton characteristic of proteins and of heterocyclic bases characteristic of nucleic acids.

Interesting effects can be expected as a result of the superposition and interaction of the system of hydrogen bonds characteristic of the polypeptide chain and the system of hydrogen bonds characteristic of nucleic acids and bases. An important structural factor, namely the hydrophobic stacking interaction between the heterocyclic bases, should also be added to the structure-forming factors playing a cardinal role in biopolymers.

In nucleopeptides the nucleic acid bases are attached to the nitrogen atom of the peptide skeleton in the 1- and 9-positions (in the pyrimidine and purine bases respectively). These are the positions at which the nucleic acid bases are attached to the pentose phosphate skeleton in polynucleotides. Thus the nucleic acid bases in nucleopeptides retain in an unchanged form all the structural elements necessary for the formation of specific mutually complementary hydrogen bonds between the complementary bases.

The distances between neighbouring nucleic acid bases in regular nucleopeptides are identical and equal to the translation along the chain by one nucleoaminoacid residue.

The combination of the above structural features of nucleopeptides creates the necessary and sufficient conditions for the occurrence of numerous intermolecular cooperative contacts between the nucleopeptide chains. These contacts must be similar to those which arise in the interaction of the corresponding polynucleotide chains. As a result of the cooperative nature of the process, each interaction of the pair of complementary bases increases the probability of subsequent contacts. Ultimately one may foresee the possibility of complementary interactions between different nucleopeptide chains, carrying complementary nucleic acid bases, corresponding to the canonical nucleoaminoacid pairs Aal-Tal (Aal-Ual), Gal-Cal, etc.

Complementary interactions of the above type can also take place intramolecularly, i.e. between different sections of the same nucleopeptide chain if the sequence of the alternating nucleoaminoacid residues in these sections of the nucleopeptide chain ensures the possibility of the formation of complementary pairs of nucleic acid bases.

The possibility of the occurrence of the analogous complementary interactions between nucleopeptide and polynucleotide chains and also between nucleopeptides and oligonucleotides is of especial interest. Complementary interactions can also take place when polynucleotides come into contact with nucleoaminoacids and short nucleopeptides.

All these factors suggest that it may become possible to employ nucleopeptide structures for the specific interference with nucleic acid–protein interactions, which play the most important role in vital phenomena.

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The Present State of Research into Organosulphur Compounds in Petroleum

N.K.Lyapina

Data on the compositions, structures, and properties of organosulphur compounds forming part of various petroleum distillates are examined. Attention is concentrated on the organosulphur compounds in high-boiling petroleum distillates. The results of studies on the individual and structural-group compositions of mercaptans, sulphides, and thiophens in various distillates of typical petroleums of the USSR are presented. Certain chemical properties of the organosulphur compounds of petroleum and the problems of their utilisation in the national economy are discussed.
The bibliography includes 114 references.

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I. INTRODUCTION

Organosulphur compounds, which have found extensive applications both in large-scale technical chemical processes and in fine organic synthesis, have been vigorously and comprehensively investigated in recent years. Natural organosulphur compounds (OSC) of petroleum origin, which consist of sulphides, thiophens, and mercaptans of different structure and molecular weight, have a wide spectrum of specific properties and can serve as starting materials for the synthesis of polyfunctional, bi- and poly-dentate compounds with still more interesting properties. It is sufficient to mention that sulphides from petroleum can be used as effective extractants for noble metals and that the sulphoxides obtained from them are highly selective extractants of many heavy metals and lanthanide elements.

However, in modern processes for the purification of petroleum products the OSC are either converted into hydrocarbons and hydrogen sulphide, or they are transformed into acid resins, or they remain in the petroleum products; in all these instances they are lost for specific applications. One of the main factors hindering the wide-scale employment of the OSC in the national economy is inadequate knowledge of their structure and properties. The interest in these compounds, which has arisen since the discovery of sulphurous petroleums, has been growing and expanding; the methods for the isolation and study of the composition of the sulphides and thiophens in individual petroleum distillates as well as data on their structure have been surveyed in reviews and monographs[1-3].

The studies in recent years (since 1975) are characterised by a combined approach to the investigation of the composition and properties of the OSC in petroleums and by an endeavour to determine the structure of the OSC of the entire distillate component of petroleum and to extend the practical applications of the OSC. Much attention has been devoted to the study of the OSC in high-boiling distillates, because the main bulk of the petroleum OSC is concentrated in the latter. These results are of considerable theoretical and practical interest for both petroleum chemistry and for the improvement of the technology of the processing of petroleum in order to increase the yield of light petroleum products. The study of the structure and properties of the OSC not only makes it possible to find applications for these substances and their derivatives but also stimulates the search for methods of synthesising them.

This review deals with studies in recent years of the structural-group compositions of the sulphides, thiophens, and mercaptans in the distillate components of typical petroleums, studies of the chemical reactions and the possible applications of the petroleum OSC discussed, and the existing schemes for the isolation of the OSC from petroleum distillates are analysed.

II. METHODS FOR THE ISOLATION AND DIFFERENTIATION OF ORGANOSULPHUR COMPOUNDS IN PETROLEUM DISTILLATES

Almost all petroleums contain between 0.01 and 10% of sulphur (S_{tot}).[4] Sulphurous ($0.5 < S_{tot} \leq 1.9\%$) and highly sulphurous ($S_{tot} > 1.9\%$) petroleums, whose contribution to the world production is ~60%, are of greatest interest. The OSC content in the petrol (40–200 °C), kerosene (150–250 °C), and gas-oil (190–450 °C) distillates is usually not more than 1.5, 5, and 10 wt.% respectively and the study of the structures and compositions of the OSC requires their preliminary concentration. Petroleum distillates are multicomponent mixtures of isomers of paraffinic, naphthenic, and aromatic hydrocarbons as well as sulphur, nitrogen, and oxygen compounds, for the isolation and separation of which complex multistage schemes involving the application of physical and physicochemical methods of differentiation are used. As physicochemical methods for the analysis and separation of organosulphur compounds have developed and improved, the schemes for their isolation have been modified. Three principal schemes for the extraction of organosulphur compounds from petroleum distillates are known (Fig.1).

The first scheme is based on the application of the adsorption method for the concentration of organosulphur compounds from petroleum distillates. The composition of the organosulphur compounds present mainly in petrol distillates (40–200 °C) has been studied by this scheme[5]. Elution chromatography on silica gel or alumina is usually employed[5-7]. When the adsorption-chromatographic method of concentration is used, the process conditions and the nature of the

sorbent and eluents can be varied within wide limits. The sulphur content in the resulting concentrates varies from 5 to 11%; the paraffinic-naphthenic hydrocarbons are then most completely separated, while organosulphur compounds—sulphides, thiophens, and mercaptans—are concentrated together with aromatic hydrocarbons. These concentrates are then subjected to further differentiation by complex formation with mercury acetate[5], low-temperature extraction (HI,[8] H_2SO_4 [9]), the formation of adducts with 1,3,5-trinitrobenzene,[8,10] gel permeation chromatography[11–15], fractionation, etc.

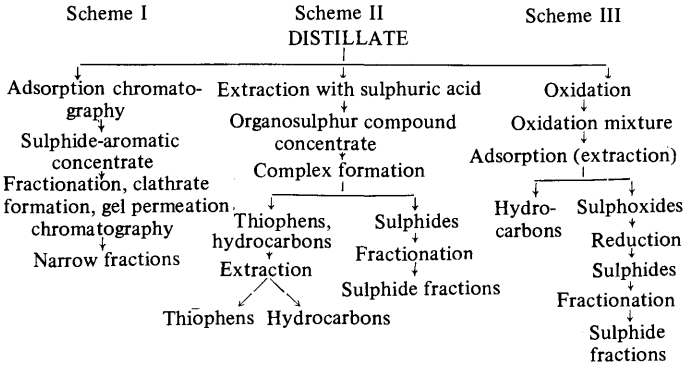


Figure 1. Schemes for the isolation and separation of organosulphur compounds in petroleum distillates.

Selective extraction is used for the preferential removal of sulphides from petroleum fractions (40–360 °C) by scheme II.[16,17] This method makes it possible to isolate from the distillate up to 70% of the sulphides, whose content in the concentrates is ≤60% in sulphuric acid extraction[16] and 40–50% in extraction by organic solvents[17]. Together with sulphides, hydrocarbons and thiophen derivatives are coextracted into the concentrates; the concentrates obtained with the aid of organic solvents are distinguished by an enhanced content of aromatic hydrocarbons. The OSC content in the sulphuric acid concentrates can be raised to 95–97% by means of re-extraction with sulphuric acid[18] or a countercurrent using another solvent[19]. For the selective extraction of sulphides from distillates and sulphuric acid concentrates of OSC, complex formation with silver nitrate is used[20], whereby one can obtain sulphides which are virtually free from thiophens and hydrocarbons. Titanium tetrachloride[21] and aluminium chloride[22] are also used as complex-forming agents; the degree of extraction of sulphur from the distillates is then low (39%), since oxygen and organonitrogen compounds are extracted together with the OSC.

Scheme II has been used[5] to identify the organosulphur compounds in petrol distillates (40–190 °C) and to establish the structural-group composition of organosulphur compounds from the middle distillates (15–360 °C) of a series of petroleums[23–25]. However, this scheme is apparently relatively inapplicable to the fraction of heavy high-tar petroleums owing to the marked charring in the sulphuric acid extraction stage and the low yield of complexes with silver nitrate.

The technology of the preparation of concentrates of organosulphur compounds from middle petroleum distillates on an experimental industrial scale has been developed on the basis of this method[26,27]. The large batches of concentrates of organosulphur petroleum compounds obtained were tested for the first time on an industrial scale in various branches of the national economy[28,29].

Scheme III, proposed[30] for the isolation and investigation of sulphides in petroleum distillates, is based on the chemical method of isolation. The authors[30] developed conditions for the selective oxidation of sulphides in a mixture with thiophens and hydrocarbons. The sulphoxides isolated are either desulphurised or reduced and the composition of the resulting hydrocarbons or sulphides is investigated; it is then possible to characterise up to 80% of the sulphides (relative to their initial content). The method is applicable to the light and middle distillates and has been used successfully for the industrial preparation of sulphoxides[31].

This scheme has been used in the investigation of the sulphides in the Romashki petroleum[32], the accumulated South Uzbekistan petroleum[33], the Khaudag and Kyzyl-Tumshuk petroleums[34], and the organosulphur compounds in the deparaffinated distillate of the Kuwait petroleum[35].

Apart from the adsorption methods for the isolation of mercaptans from petroleum distillates, methods involving extraction with 40% alkali[36], sodium aminoethoxide in anhydrous ethylenediamine[37], and the metal oxides and salts[38] are widely used. The degree of extraction of mercaptans is low (up to 40%) when mercury chloride, mercury acetate, cadmium acetate, and silver nitrate are used[38], about 60% for extraction with an ethanol solution of 40% KOH,[36] 68% for extraction with sodium aminoethoxide[37], and up to 96% for extraction with iron dodecarbonyl[39]. Mercaptans are regenerated from the mercaptides or disulphides obtained by these methods in order to investigate their structural-group composition. After demercaptanisation, the residual OSC in the distillates are isolated in accordance with schemes I and II (Fig. 1).

Sometimes the order of treatment can be altered. Thus, in the study of mercaptan-containing distillates, adsorption is carried out initially and then alkaline extraction, etc.[8] It is noteworthy that repeated treatment with reagents is usually necessary. Depending on the aim, fractionation, molecular distillation[8], thermal diffusion separation[40], etc. are used in various stages.

Concentrates of thiophens, sulphides, and mercaptans or narrow fractions are investigated by a set of various physical methods of analysis, including infrared and ultraviolet spectroscopy, ^{1}H NMR, mass spectrometry, hydrodesulphurisation on Raney nickel, gas–liquid chromatography, chemical reactions, and elemental and functional analyses in order to identify the components and determine the structural-group composition.

III. INVESTIGATION OF THE COMPOSITIONS OF CONCENTRATES OF ORGANOSULPHUR COMPOUNDS IN PETROLEUM DISTILLATES

The study of the composition of the OSC has been developing in three main directions: (1) group analysis of the OSC in petroleums and petroleum products; (2) identification of the OSC, which is characteristic of studies of the OSC in the petrol–ligroin distillates (40–240 °C); (3) determination of the structural-group composition of the OSC, which is most widely used in the study of the kerosene–gas-oil distillates (150–535 °C).

1. The Group Composition of Petroleum OSC

The analysis of the group composition of the OSC in petroleums and distillates involves the determination of elemental (S_S), hydrogen sulphide (S_{H_2S}), mercaptan (S_{merc}), disulphide (S_{RSSR}), and sulphide (S_{sulph}) sulphur. The unidentified component is usually referred to as the

residual or thiophen sulphur (S_{res}); it usually constitutes a large fraction, owing to the difficulties arising in the analysis and the study of the composition and structure of the petroleum OSC. The residual sulphur includes (apart from that in thiophens) the sulphur in diaryl and alkyl aryl sulphides, but only a small amount of these compounds has been found in petroleums[13].

Hitherto systematic studies have been made of the group compositions of the OSC present in the distillates (40–300 °C) for the majority of the petroleums in the USSR (250 specimens of petroleums and distillates boiling up to 300 °C),[43] America, and the Near East[4]. These data are necessary for the technological characterisation of sulphurous and highly sulphurous petroleums. However, the existing methods for the analysis of the group composition of the OSC have been developed for the low-boiling and middle distillates and are inapplicable to the high-boiling distillates (above 360 °C), a characteristic feature of which is the similarity and averaging of the properties of the components.

The results of the study of the group composition of the OSC of certain petroleums are presented in Table 1. Depending on the group composition of the OSC contained in the distillates, petroleums can be divided by convention into three types: thiophen petroleums (type I), which contain mainly thiophen sulphur and not more than 10% of sulphide sulphur, while the remaining groups are absent; sulphide petroleums (type II) containing thiophens and sulphides, while the content of mercaptans is not more than 5%; mercaptan petroleums (type III), which contain comparable amounts of sulphides, thiophens, and mercaptans and there is also a possibility of the presence of disulphides, hydrogen sulphide, and elemental sulphur (see Table 1). Since the content of hydrogen sulphide in petroleum is variable and depends on the sampling, storage, and transport conditions, its amount in petroleum is usually not determined. Petroleums of the first and third types are encountered in nature much more rarely than those of the second type.

Table 1. The group compositions of the organosulphur compounds in certain world petroleums (relative content, %).

Petroleum	Refs.	S_{tot}	S_{res}	S_{sulph}	S_{merc}	S_{RSSR}	S_S
Type I							
Usinsk, USSR	[41]	2.07	100	0.00	0.00	0.0	0.00
Yaregsk, USSR	[42]	1.11	100	0.00	0.00	0.0	0.00
Ust'-Balyk, USSR	[43]	1.45	89.0	11.0	0.00	0.0	0.00
Type II							
Santa Maria, California	[4]	4.99	58.20	41.6	0.20	0.0	0.00
Wester Surgut, USSR	[44]	3.00	68.5	31.5	0.00	0.0	0.00
Arlansk, USSR	[45]	1.02	70.0	30.0	0.00	0.0	0.00
	[23]	3.05	76.17	23.6	0.23	0.0	0.00
Type III							
Terekli, USSR	[43]	2.27	81.8	8.8	9.07	0.0	0.29
Orenburg, USSR	[46]	2.33	84.5	7.2	8.30	0.0	0.00
Wasson, Texas	[4]	1.85	52.5	24.6	15.3	7.4	0.10
Deep River, Michigan	[4]	0.58	28.6	3.0	45.9	22.5	0.01

Each of the above types of petroleum is not characterised solely in terms of differences between their group compositions. The thermal stability of the petroleum OSC is an important technological characteristic[43], decreasing on passing from petroleums of type I to those of type III, which must be taken into account in the study of the composition and structure of the OSC. The content of sulphur in all the consecutively boiling fractions of petroleums of types I and II is higher the higher its content in the petroleum. The sulphur content in the low-boiling distillates of petroleums of type III can be higher than in the high-boiling distillates and depends mainly on the thermal stability of the OSC. The group compositions of straight-run distillates (particularly petrol distillates) of petroleums of various types therefore differ greatly (Table 2). With increase of the boiling point of the distillate, the difference is smoothed out.

Table 2. The proportions of organosulphur compounds in the distillates of certain petroleums.

Sulphur	Boiling range of distillate, °C		
	40–200	200–360	360–410
Type I (Usinsk) (Ref.41)			
Overall, wt.% of distillate (*A*)	0.06	0.93	1.15
Overall, % of total sulphur in petroleum (*B*)	0.2	9.5	4.5
Sulphide, % of total sulphur in distillate (*C*)	25	—	—
Thiophen, % of total sulphur in distillate (*D*)	75	100	100
Type II (Western Surgutsk) (Ref.44)			
A	0.16	2.0	3.0
B	0.83	23.2	9.2
C	96	60	47
D	4	40	53
Type III (Orenburg) (Ref.46)			
A	0.53	1.1	1.7
B	10.9	30.0	13.6
E *	52.0	16.0	6.0
C	39.0	24.0	12.5
D	9.0	60.0	81.5
Type III (Markovsk) (Ref.43)			
A	0.96	0.73	—
B	29.9	16.1	

*Mercaptan sulphur, % of total sulphur in distillate.

It is noteworthy that active sulphur compounds (S, H_2S, RSH, RSSR) are mainly concentrated in the low-boiling distillates.

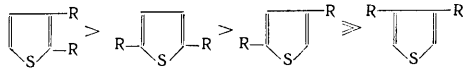
2. Identification of Petroleum OSC

The identification of the OSC in petroleum distillates is a fairly complex problem, as a result of which only 200 organosulphur compounds have been identified in the course of 90 years[5,8]. The results of the identification permit the conclusion that, in the petrol distillates (40–200 °C) of type I petroleums, the OSC consist of alkylthiophens and their derivatives, those in type II petroleums are mainly cyclic sulphides, and those in type III petroleums are aliphatic and cyclic mercaptans and sulphides. All the potential isomers of the sulphides and mercaptans, ranging from C_3 to C_7 (with the exception of unstable compounds containing less than 4 carbon atoms in the ring), are present in these distillates of petroleums of the first and second types. The majority of monocyclic sulphides in petroleums consist of alkylthiacyclopentanes and alkylthiacyclohexanes, the amount of the latter

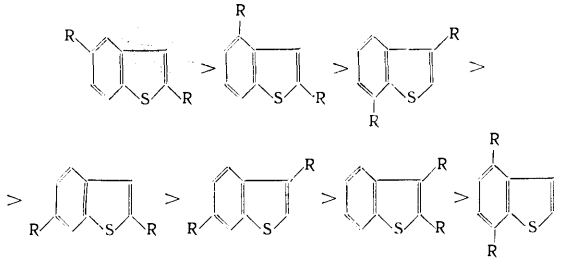
being smaller by a factor of ~2 (which follows from the analysis of the literature data[47-50]). *gem*-Substituted, α,β-disubstituted (in five- and six-membered sulphides), and α,β,γ-trisubstituted (in six-membered sulphides) are more rarely encountered among cyclic sulphides.

The main bulk of the branched aliphatic sulphides and mercaptans as well as paraffins isolated from the distillates consist of isomers with a single branch in the hydrocarbon group[47,48]. Compounds with groups located in the α- and β-positions relative to the sulphur atom are usually encountered. The number of isomers with two branches in the group is much smaller and those with three and more branches have not so far been detected[47-51].

Among the identified C_4–C_7 alkylthiophens[50,51] and C_8–C_{11} benzothiophens[7,8,52-57], the α-derivatives are usually encountered, the isomers of the disubstituted thiophens forming the following sequence in terms of their relative contents in petroleum:



while disubstituted benzothiophens give rise to the sequence



Eighteen C_8–C_{11} alkylthiaindans, mainly with methyl and ethyl substituents, have been identified. The substituents are usually located in the 2- and 3-positions relative to the sulphur atom[6].

Identification made it possible to characterise the OSC in the low-boiling petroleum distillates and to deduce the most likely structures of the compounds in the high-boiling distillates. However, one should note that it is at present impossible to carry out an exhaustive identification of the OSC in the kerosene–gas-oil distillates (150–450 °C). Qualitative identification of certain successfully isolated components from the distillates does not allow inferences about the composition and properties of the mixture of OSC in the concentrates. Therefore the study of the quantitative structural-group composition of the OSC is the most valuable procedure and the only one available procedure for kerosene–gas-oil distillates.

3. The Structural-Group Composition of the Petroleum OSC

The structural-group composition of the OSC has been determined for the 150–250°, 190–360°, 360–450°, and 370 to 535 °C distillates of various petroleums of the USSR,[23,41-46] America, and the Near East.[8,11-15] The majority of the petroleums investigated belong to the second type, whose OSC consist mainly of sulphides and thiophens.

(a) The structural-group composition of the OSC of the distillates of type I petroleums. The typical structures of the OSC found in petroleums of this type are given below:

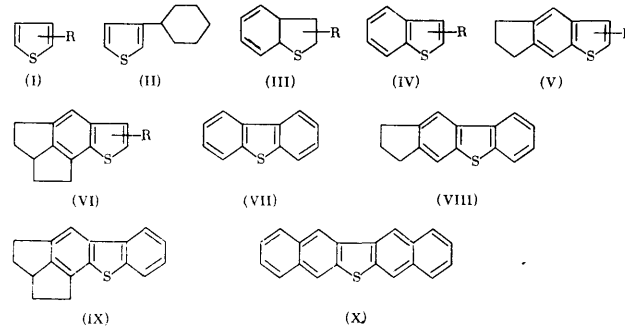


Table 3. The structural-group composition of the OSC in the high-boiling distillates of type I petroleums (relative content, %).

Type of structure	Yaregsk (Ref.42), 280–400°	Usinsk (Ref.41), 200–410°	Recluse (Ref.8)*, 370–535°	Swan Hills (Ref.8)*, 370–535°
(I)	6.4	7.0	—	—
(II)	—	0.6	—	—
(III)	5.9	12.8	—	—
(IV)	24.4	23.1	14.4**	18.6**
(V)	16.2	10.7	21.1	12.3
(VI)	10.2	9.9	—	6.1
(VII)	15.4	17.7	6.7	5.2
(VIII)	20.6	9.1	10.0	12.3
(IX)	0.5	7.4	7.8	4.9
(X)	0.4	1.7	6.7	2.3

*The sum of the high-molecular-weight thiophens is 33.3 and 38.3% for the Recluse and Swan Hills petroleums respectively.
**Calculated from the data of Rall et al.[8]

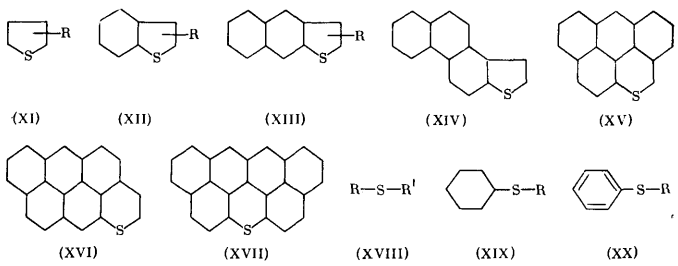
Table 3 shows that the structural-group compositions of the OSC of the 200–410 °C distillates of type I petroleums are fairly close[41,42]. Alkylbenzothiophens (IV) constitute one-fourth of the OSC. Cycloalkano- and bicycloalkano-derivatives of benzothiophens [(V) and (VI)] and dibenzothiophens [(VIII) and (IX)] constitute an appreciable fraction. Thus the content of the tricyclic and polycyclic structures (V)–(X) in these distillates is 55–65%. The contents of dibenzothiophens (VII) and their derivatives (VIII)–(X) are particularly high in the heavy Yareg petroleum[42]. A low content of alkylthiophens (I) (4–6%) and thiaindans (III) (8–10%) is characteristic of petroleums of type I.

The distillates of type I petroleums do not contain compounds with the sulphide structure probably owing to the catalytic transformations of the petroleum OSC under the influence of the petroleum-bearing rocks and the increased radioactivity of petroleum waters[42].

The content of thiophen structures increases with increasing boiling point of the distillate, the quantitative content of benzothiophens, dibenzothiophens, and cycloalkanodibenzothiophens increasing faster than that of alkylthiophens and cycloalkano- and bicycloalkano-benzothiophens. These data, characterised by an increased content of aromatic OSC, agree with the hydrocarbon composition of the distillates,

which are distinguished by a higher content of naphthalene and phenanthrene hydrocarbons.

(b) The structural group composition of the OSC in the distillates of type II petroleums. The typical structures of the sulphides detected in these petroleums are as follows:



With increase of the boiling points of the distillates, the content of sulphides in the OSC diminishes (Table 2). The sulphide component of the OSC in the petrol distillates (40–190 °C) of the Weatern Surgut petroleum consists of almost 90% of thiacycloalkanes. The fraction of thiamonocycloalkanes (XI) is 80%, while the content of thiabicycloalkanes (XII), thiaindans (III), and dialkyl sulphides (XVIII) does not exceed 5–7%.[58]

Thiamonocycloalkanes also predominate (45–55%) in the diesel distillate (190–360 °C) of this petroleum, but their relative content is smaller by ~20–30% than in the petrol distillate. The number of rings in the thiacycloalkane molecules in this distillate increases to 4–5. The content of dialkyl sulphides is reduced by a factor of ~2, while the content of thiaindans remains unchanged[44].

Thiamonocycloalkanes predominate in the 360–410 °C distillate, while the content of thiabicycloalkanes is fairly high[59]; the latter predominate in the 410–450 °C distillate[60]. These data show that the number of rings in the OSC molecules increases with increasing boiling point of the distillate.

Thus the relative content of thiamonocycloalkanes and dialkylsulphides falls on going from a low-boiling to a high-boiling distillate, the content of thiaindans changes little, and that of thiapolycycloalkanes increases.

The absolute content of all types of sulphides in the distillate as a rule increases with increase of the boiling point (Fig.2).[61] The absolute content of thiamonocycloalkanes is a maximum in the 360–410 °C distillate and that of acyclic sulphides is a maximum in the 190–360 °C distillate. The curve representing the proportions of thiamonocycloalkanes as a function of the boiling point of the distillate has a lower slope than the corresponding curves for thiabi-, thiatri-, thiatetra-cycloalkanes, which means that the increase in the number of rings in the molecules of the organosulphur compounds is faster than the increase in the size of the molecules with increase of the length of the alkyl group in the alkylcycloalkane.

Polynuclear OSC with a long side chain or with a naphthene ring as substituents have not been discovered in the 190° to 360 °C distillates. This may be evidence that the increase in molecular weight is to a large extent associated with the increase of the degree of substitution.

In contrast to sulphides, the content of thiophens increases and becomes dominant in the high-boiling distillates. For example, alkylthiophens (100%), constituting 2–4% of the total content of the OSC, have been found in the petrol distillate (40–200 °C) of the Western Surgut petroleum. The dominant structural group in the thiophen component of the 190–360 °C distillate[44] is alkylbenzothiophens (60–80%), while alkylthiophens constitute not more than 5–7%. The thiophen components of the 360–410° and 410–450 °C distillates[59,60] contain mainly alkylbenzothiophens (~40%) and cycloalkanobenzothiophens (16%). The absolute content of alkylthiophens is a maximum in the 360–410 °C distillate: on passing to the high-boiling distillate, the content of cycloalkanobenzothiophens and dibenzothiophens increases most sharply; the amount of the remaining structural groups of thiophens increases uniformly (Fig.3).[61]

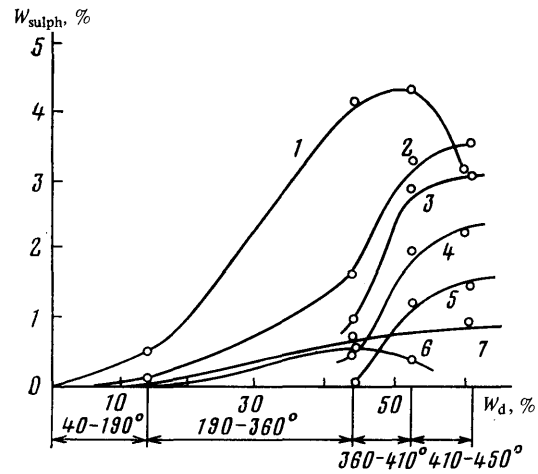


Figure 2. The proportions of thiamonocycloalkanes (curve *1*), thiabicycloalkanes (curve *2*), thiatricycloalkanes (curve *3*), thiatetracycloalkanes (curve *4*), thiapentacycloalkanes (curve *5*), dialkyl sulphides (curve *6*), and thiaindans (curve *7*) in the 40–190°, 190–360°, 360–410°, and 410–450° distillates of the Western Surgut petroleum (W_d = yield of distillate, wt.% of petroleum; W_{sulph} = content of sulphides, wt.% of the corresponding distillate).

The quantitative contents of the structural groups of sulphides and thiophens in the high-boiling distillates of various type II petroleums are compared in Table 4. It is noteworthy that the compositions of thiacycloalkanes are similar, the differences between the relative contents of alkylthiabi-, alkylthiatri-, and alkylthiatetra-cycloalkanes being particularly small. The increased content of thiamonocycloalkanes and the reduced content of thiapolycycloalkanes in the Wester Surgut petroleum, compared with the other petroleums quoted, is consistent with the differences between the boiling points of their distillates. Compared with the sulphide component of the OSC, the structural-group compositions of the thiophen components of these petroleums differ to a greater extent.

The results of the estimates of the overall contents of the individual structural groups in straight-run distillates (40–450 °C) are presented in Fig.4. Evidently the structural groups present in greatest amounts comprise alkylbenzothiophens and thiamono-, thiabi-, and thiatri-cycloalkanes; the sum of the acyclic sulphides is 5%.[61] The relative content of compounds with increasing numbers of rings in their molecules diminishes uniformly for thiacycloalkanes and non-uniformly for thiophens. The diagram shows that the content of alkylbenzothiophens greatly exceeds that

of all the remaining thiophen groups. This can apparently be accounted for by the higher stability of alkylbenzothiophens and the possibility of the presence of a large amount of isomers. Some of the alkylbenzothiophens are probably the products of the thermal degradation of the more condensed thiophen-containing polynuclear structures.

(c) The structural-group composition of the OSC of type III petroleums. A considerable amount of OSC (S_{tot} = 0.53) has been found in the low-boiling distillates of petroleums of this type, exceeding by an order of magnitude that in the analogous distillates of type I and II petroleums.

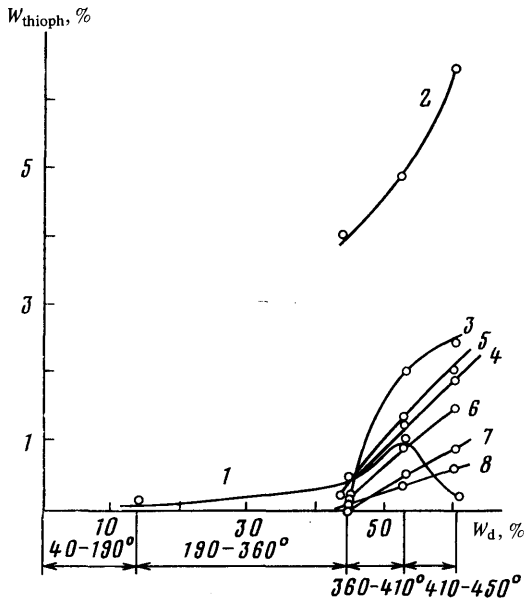


Figure 3. The proportions of alkylthiophens (curve *1*), alkylbenzothiophens (curve *2*), alkylcycloalkanobenzothiophens (curve *3*), bicycloalkanobenzothiophens (curve *4*), dibenzothiophens (curve *5*), cycloalkanodibenzothiophens (curve *6*), thienophenanthrenes (curve *7*), and dicycloalkanothienophenanthrenes (curve *8*) in the 40–190°, 190° to 360°, 360–410°, and 410–450° distillates of the Western Surgut petroleum (W_d = yield of distillate, wt.% of petroleum; W_{thioph} = content of thiophens, wt.% of the corresponding distillate).

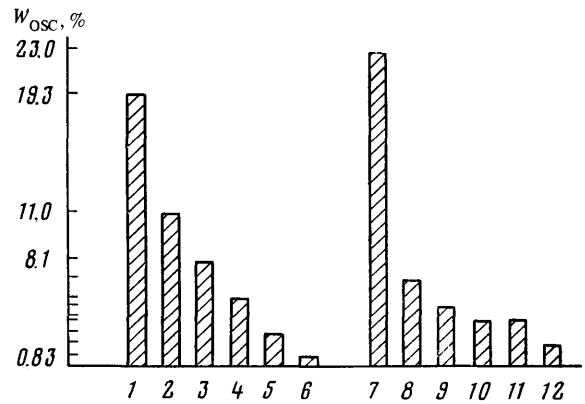


Figure 4. The proportions (% of total OSC) of thiamonocycloalkanes (column *1*), thiabicycloalkanes (column *2*), thiatricycloalkanes (column *3*), thiatetracycloalkanes (column *4*), thiapentacycloalkanes (column *5*), thiahexacycloalkanes (column *6*), alkylbenzothiophens (column *7*), cycloalkanobenzothiophens (column *8*), bicycloalkanobenzothiophens (column *9*), thiaindans (column *10*), dibenzothiophens (column *11*), and alkylthiophens (column *12*) in the 40° to 450 °C distillates of the Western Surgut petroleum.

Table 4. The content (wt.% of petroleum) of the principal structural groups of thiophens and thiacycloalkanes in 370–535 °C high-boiling distillates of type II petroleums.

Type of structure	Prudhoe Bay*	Gach-saran*	Wilmington*	Western Surgut** (Ref.57)
(I)	—	—	0.017	0.015
(II)	—	—	0.027	0.015
(IV)	0.18	0.33	0.20	0.50
(V)	0.10	0.24	0.17	0.19
(VI)	0.07	0.17	0.13	0.15
(VII)	0.26	0.35	0.31	0.16
A***	0.59	0.47	0.63	0.18
(XI)	0.052	0.245	0.193	0.23
(XII)	0.150	0.269	0.272	0.26
(XIII)	0.190	0.262	0.286	0.23
(XIV)	0.160	0.250	0.202	0.17
(XV)	0.119	0.256	0.207	0.06
(XVI)	0.065	0.193	0.195	0.05
(XVII)	0.050	0.250	0.185	—

*Calculated from the data of Rall et al.[8]
**410–450 °C distillate.
***A = sum of high-molecular-weight thiophens.

With increase of the boiling point of the distillate, the content of mercaptans and sulphides falls, while that of thiophens increases (Table 2). The content of mercaptans decreases more than that of the sulphides. The absolute content of mercaptans is a maximum in the 200–360 °C distillate. The mercaptans in the low-boiling distillates are mainly primary or secondary. The 200–360 °C distillate contains a very large amount of cyclic mercaptans[62].

The sulphides consist mainly of thiamonocycloalkanes and acyclic sulphides (Fig.5). It is noteworthy that, in contrast to the corresponding distillates of type II petroleums, these distillates contain a considerable amount of dialkyl sulphides and alkyl cycloalkyl sulphides[46]. Among thiophens, dibenzothiophens predominate, particularly in the 200–360 and 360–410 °C distillates. The content of alkylthiophens is slight[62]. The curves illustrating the relative contents of dibenzothiophens as well as cycloalkano- and bicycloalkanobenzothiophens in the distillates become steeper with increase of the boiling points of the latter than the corresponding curves for benzothiophen and particularly alkylthiophen derivatives. These results show that the amount of condensed OSC molecules increases sharply with increase of the boiling point of the distillate. Thus type III petroleums are similar to type I petroleums in terms of the structural-group composition of the thiophens and the nature of their distribution among the distillates and can serve as the starting material for the preparation of benzo- and dibenzo-thiophens.

4. Certain Generalisation Concerning the Individual and Structural-Group Compositions of the OSC of World Petroleums

On the basis of the results of the identification [of components] and the study of the structural group-composition of the OSC of the petrol, kerosene, and gas-oil distillates, it is possible to make certain comparisons and generalisations. The principal components of the 40–535 °C distillates are benzo- and dibenzo-thiophens in petroleums of the thiophen type, thiacycloalkanes and benzothiophens in petroleums of the sulphide type, and dibenzothiophens, thiacycloalkanes, acyclic sulphides, and mercaptans in petroleums of the mercaptan type.

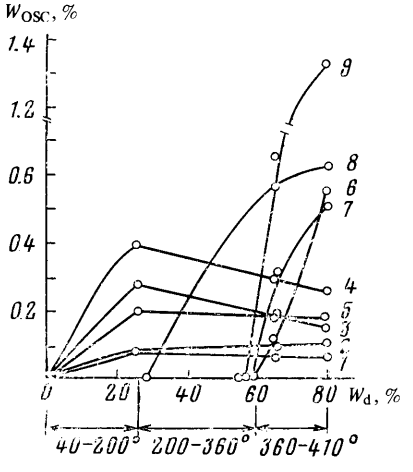


Figure 5. The proportions of alkyl cycloalkyl sulphides (curve *1*), thiaindans (curve *2*), dialkyl sulphides (curve *3*), thiamonocycloalkanes (curve *4*), alkylthiophens (curve *5*), cycloalkanobenzothiophens (curve *6*), bicycloalkanobenzothiophens (curve *7*), benzothiophens (curve *8*), and dibenzothiophens (curve *9*) in the 40–200°, 200–360°, and 360° to 410 °C distillates of the Orenburg petroleum (W_d = yield of distillate, wt.% of petroleum; W_{OSC} = OSC content, wt.% of the corresponding distillate).

The thiacycloalkanes consist mainly of five- and six-membered isomers. The number of rings increases with increasing boiling point of the fraction. The maximum content of isomers with the greatest number of substituents is characteristic of thiamonocycloalkanes, the substituents being linked to different carbon atoms. The kerosene distillate (150–250 °C) contains 25% of α,α'-dialkylthiamonocycloalkanes with substituents having the straight-chain structure only, while the diesel distillate (190–360 °C) contains ~5% of similar structures relative to the total amount of thiamonocycloalkanes[23].

A detailed comparison of the structural-group compositions of the sulphides isolated from diesel distillates (190–360 °C) with petroleums of the sulphide type shows that they are qualitatively similar (Table 5). The quantitative contents of the individual structural groups in the distillates of highly sulphurous petroleums (for example the Arlansk and Western Surgut petroleums) are approximately the same; the corresponding structural groups are present in a smaller amount in the distillates of sulphurous petroleums (the Samotlor petroleum). However, the relative contents of analogous structures are fairly similar in distillates of petroleums of the same type. Thus the contents of the principal components (thiamono- and thiabi-cycloalkanes) differ by not more than 15–20%. This result is important for the practical utilisation of petroleum sulphides.

Table 5. The structural-group composition of the sulphides in the 190–360 °C distillates of type II petroleums (relative content, %).

Type of structure	Petroleum					
	Arlansk (Ref.23)	Western Surgut (Ref.44)	Samotlor (Ref.45)	South Uzbek (Ref.33)*	Khaudag (Ref.34)*	Kyzyl-Tumshuk (Ref.34)*
(III)	4.71	3.30	3.20	6.4	3.6	2.8
(XI)	45.58	56.0	57.58	59.4	59.2	53.0
(XII)	20.99	16.6	20.96	19.7	25.0	24.0
(XIII)	12.66	13.0	8.54	8.7	10.4	9.4
(XIV)	4.71	5.40	2.44	1.9	1.3	3.6
(XVIII)	6.94	3.1	3.66	1.7	0.5	4.7
(XIX)	2.99	3.2	3.12	2.2	—	2.5
(XX)	1.42	—	0.50	—	—	—

*Calculated from data in Refs.33 and 34.

Comparison of the quantitative contents of the individual structural groups of thiophens in different petroleums revealed certain characteristic features. Benzothiophens predominate in the distillates of highly sulphurous type II petroleums[9]. Both thiophens and benzothiophens and naphthenobenzothiophens have been found in approximately equal amounts in the distillates of sulphurous petroleums of this type[45]. Condensed derivatives of benzo- and dibenzothiophens greatly predominate in the distillates of type I and III petroleums.

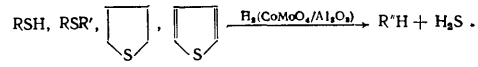
It follows from the data presented above that the relative contents of the individual and structural groups of OSC within the limits of each class (sulphides, thiophens, benzothiophens, and naphthenobenzothiophens) are approximately of the same order of magnitude for different petroleums, as in the case of hydrocarbons[63]; the contents of each class of compounds in different petroleums are different.

The data presented permit the conclusion that certain petroleum distillates can serve as a realistic source of natural mercaptans, thiacycloalkanes, benzothiophens, dibenzothiophens, etc.

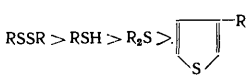
IV. CHEMICAL PROPERTIES OF THE MERCAPTANS, SULPHIDES, AND THIOPHENS IN PETROLEUM

The petroleum OSC consist of a mixture of isotypical structures of different molecular weights, the functionality of the molecules decreasing as a rule with increasing molecular weight. One can therefore postulate that only those reactions which exhibit a low selectivity within the homologous series and are at the same time highly sensitive to the functional characteristics of the molecules can be used successfully in the chemistry of petroleum OSC. This is why only a few of the known reactions of individual mercaptans, sulphides, and thiophens have been applied to petroleum systems.

The reaction most thoroughly investigated in this sense is that of hydrogenolysis—one of the most effective methods for the desulphurisation of all the groups of OSC:



The catalysts for the hydrodesulphurisation of the OSC are cobalt, molybdenum, tungsten, nickel, and iron oxides or sulphides or their mixtures on alumina. The process is carried out under a hydrogen pressure from 4 to 70 atm at 300–425 °C (depending on the composition of the OSC and their content in the petroleum products)[64]. In terms of their capacity to undergo hydrodesulphurisation, the OSC can be arranged in the sequence

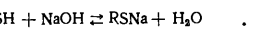


Depending on the conditions, the process can be carried out with a quantitative conversion of the OSC. More severe conditions are required in the hydrodesulphurisation of compounds with a high molecular weight and a large number of rings in their molecules and with a high degree of condensation. Hydrogenolysis has been widely used in industrial large-scale processes involving the removal of sulphur from petroleum products and also in analytical practice.

The reactions characteristic of specific groups of OSC are examined below.

1. Reactions of Petroleum Mercaptans

Mercaptans are the most reactive compounds among the OSC; they exhibit acidic properties and react fairly readily with alkalies:

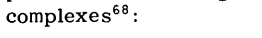


The reaction is reversible and mercaptans can be regenerated by hydrolysis and for this reason the degree of conversion is low even for low-boiling mercaptans. Aliphatic mercaptans react more readily the shorter their hydrocarbon chain and the lower the degree of branching of the latter. The addition of the so-called "solutisers" increases the degree of conversion. The solutisers tested have included *m*- and *p*-cresols, phenol, ethanol, and methanol[65,66]. The use of the latter makes it possible to achieve a virtually theoretical conversion of mercaptans (90–95%). However, after regeneration the yield of mercaptans does not exceed 60%,[66] because they are readily oxidised by atmospheric oxygen to disulphides. A high degree of extraction of petroleum mercaptans (40–60%) is observed when they are treated with a KOH solution containing monoethanolamine[36]. The subsequent oxidation of the resulting mercaptans to disulphides takes place in the presence of catalysts—copper(I) chloride or the sodium salt of cobalt-disulphophthalocyanine ($C_{32}H_{14}O_6N_8S_2CoNa_2$):



The method makes it possible to remove mercaptan sulphur almost completely from petrols[66], light hydrocarbon fractions, and gas condensates[67].

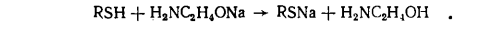
Disulphides can be formed in acetic acid solution in the presence of lead tetra-acetate[3] and in concentrated sulphuric acid. Mercaptans are capable of substituting the carbonyl groups in iron carbonyl complexes[68]:



The relative reactivities of the OSC form the sequence (in proportions of 14 : 9 : 1)

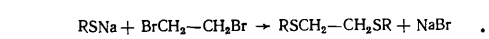
Mercaptans react most fully with iron dodecarbonyl, forming iron tricarbonyl mercaptides. When dry hydrogen chloride is passed through iron tricarbonyl mercaptides in solution in dodecane at elevated temperatures, the corresponding mercaptans are formed. Treatment of this solution with copper(II) chloride makes it possible to obtain the disulphides. Oxidation with concentrated nitric acid leads to a quantitative yield of the corresponding alkanesulphonic acid (isolated as the sodium salt)[68]. The sodium salts of sulphonic acids can be obtained by the oxidative chlorination of petroleum mercaptans followed by hydrolysis with alkali[69].

Petroleum mercaptans react with heavy metal oxides and salts. The reactions with silver nitrate[38], cadmium acetate and chloride[65], and mercury acetate[66] have been investigated; in all cases the degree of conversion of the mercaptans is low (~60–70%). In the reaction with mercury acetate the tertiary mercaptans decompose with dissociation of the C–S bond. The reaction with sodium aminoethoxide in anhydrous ethylenediamine is less sensitive to the structural features of mercaptans[37]:



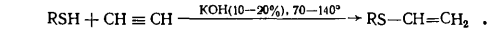
The degree of conversion of the mercaptans is almost quantitative.

Bis-sulphides have been obtained by the reaction of petroleum mercaptans with 1,2-dibromoethane:

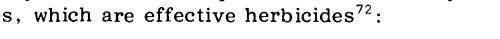


The reaction proceeds in an alcoholic solution of alkali and the yield of bis-sulphides is 75–85%,[70] the products being effective stabilisers in the thermo-oxidative degradation of poly(methyl methacrylate).

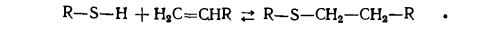
Petroleum mercaptans constitute a readily available starting material for the synthesis of vinyl sulphides[71];



The reaction is quantitative and the products can be used as insecticides, flotation agents, and as a base for varnishes. The condensation of mercaptans in the petrol and kerosene distillates with ethylene chlorohydrin followed by oxidation and dehydration makes it possible to obtain alkyl vinyl sulphones, which are effective herbicides[72]:



Petroleum mercaptans react fairly completely with olefins[73,74]:



The C–C bonds in olefins were thi-ylated with the mercaptans of the low-boiling fraction (40–200 °C) of the Orenburg petroleum containing 0.22 wt.% of mercaptan sulphur and 0.25 wt.% of sulphide sulphur[62]. The catalysts used were benzoyl peroxide, aluminium chloride, ethylenealuminium dichloride, and an aluminium-containing catalytic complex. The results indicate a fairly high degree of conversion of the petroleum mercaptans (70–80%). Among the olefins investigated, best results were obtained for 2-methylpent-1-ene, containing an active carbonium ion attached to the double bond, and the best catalysts were ethylenealuminium dichloride and the active aluminium-containing complex. Analysis of the group composition of the product agreed satisfactorily with the results of the physicochemical study of the sulphide concentrate isolated from this fraction by extraction with

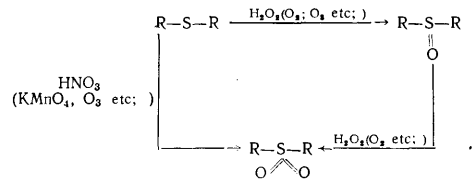
sulphuric acid. Comparison of the structural-group compositions of the sulphides present in the petrol distillate and obtained from the petroleum mercaptans shows that the main bulk of the former sulphides have a lower molecular weight than those obtained from the mercaptans[62].

A lower degree of conversion is characteristic of the interaction with olefins of the mercaptan concentrate obtained from the higher-boiling distillate (200–360 °C) in which the content of mercaptan sulphur is 8.25%.[62] This can apparently be accounted for by the lower thi-ylating activity of cyclic mercaptans, ~30% of which were detected in the given concentrate relative to the total OSC content. Among the olefins tested, low-molecular-weight olefins, namely isoprene and 2-methylpent-1-ene, proved to be the most reactive in the reaction with mercaptans[62,74]. Investigations have shown that aliphatic mercaptans can be converted almost quantitatively into sulphides, which can be more conveniently isolated and their structural-group composition investigated, because, as shown above, mercaptans are oxidised during isolation and intense corrosion of the detector is observed in analysis by gas–liquid chromatography (GLC).

The possibility of the catalytic conversion of petroleum mercaptans into sulphides makes it possible to regard mercaptan-containing petroleums and gas condensates as additional sources of raw materials for the preparation of sulphides.

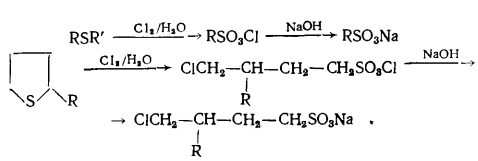
2. Reactions of Petroleum Sulphides

Reactions involving the oxidation of petroleum sulphides to sulphoxides and sulphones have been vigorously investigated in the last 10–15 years:

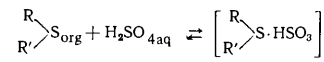


The oxidants used in these reactions are hydrogen peroxide[2,75], atmospheric oxygen in the presence of transition metals and their oxides and sulphides[76], heteropolyacids[77], organic hydroperoxides, etc. The highest selectivity and highest degree of conversion are attained when the reaction is carried out at 70–80 °C in the presence of catalytic amounts of H_2SO_4. The yield of sulphoxides is 70–80%.[2] Depending on the conditions, the oxidation can be continued until the formation of sulphones in 90–100% yields. Sulphides with a higher molecular weight are oxidised under more severe conditions. This reaction is very important for the preparation of substances with biological activity[78] and complex-forming capacity[79], i.e. substances with more valuable properties than the initial petroleum sulphides.

Different fractions of sulphides isolated from distillates of highly sulphurous petroleums readily undergo oxidative chlorination. Subsequent hydrolysis of the reaction products yields the sodium salts of sulphonic acids[80]:



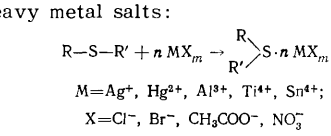
Sulphuric acid has been used for a long time for the removal of OSC from petroleum products. It has been established that the interaction of petroleum sulphides with sulphuric acid is exothermic[18,81] and results in the formation of a protonated complex:



The degree of protonation depends on the molecular weight and structure of the sulphide, the sulphuric acid concentration, and the extraction temperature. With increase of the molecular weight of the sulphide, protonation takes place at a lower temperature and with more concentrated acid[9,82].

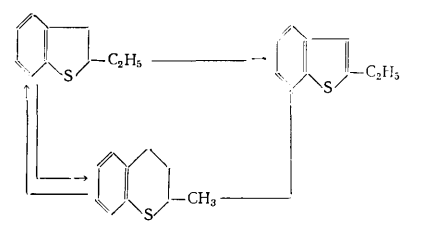
Apart from sulphuric acid, HI,[83] HF,[55] and copper sulphate dihydrochloride[84] have been tested as protonating agents: the first two reagents have not found extensive application owing to the occurrence of side reactions (the dissociation of the C–S bond in sulphides with a tertiary carbon atom in the α-position relative to the sulphur atom, coextraction of aromatic hydrocarbons, and the predominance of the reaction with aromatic hydrocarbons) and the difficulty of regenerating the extracted sulphides. Copper sulphate dihydrochloride is a milder protonating agent, which is active in reactions with low-molecular-weight sulphides.

Petroleum sulphides undergo fairly readily addition reactions with heavy metal salts:



It has been established that, with increase of molecular weight and with decrease of the symmetry of the sulphides, their reactivity falls[85]. Mercury derivatives have therefore been obtained mainly for the sulphides in the petrol–ligroin distillates[5]. Titanium[86] and aluminium[87] salts proved to be less selective complex-forming agents, since they react vigorously also with other hetero-organic compounds containing nitrogen and oxygen.

The catalytic dehydrogenation and isomerisation of thia-heterocycloalkanes of different structure are promising reactions:



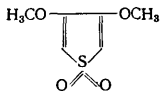
It has been shown[88] that the reaction proceeds via an ionic mechanism involving the successive elimination of a hydride ion and a proton. It has been found that the reactions are effective in the presence of quinoline-treated ASK-Na or ASK catalysts.

3. The Reactions of Petroleum Thiophens

Despite the considerable content of thiophens of different structure in petroleums, their compositions and properties have been less thoroughly investigated than those of sulphides and mercaptans. This is probably due to the difficulty of isolating them from a mixture with aromatic hydrocarbons and other sulphur compounds and the fact that their

main bulk is present in the relatively little studied high-boiling petroleum distillates.

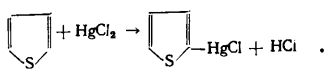
Thiophens are more resistant to oxidation than sulphides. The introduction of electron-donating substituents into the thiophen molecule promotes its oxidation to the sulphone[89]. Stable sulphones are formed in the presence of two symmetrically located substituents:



On treatment with strong oxidants, the side chains are converted into carboxy-groups. As regards the degree of oxidation of petroleum thiophens, the available literature data do not permit a clear-cut analysis, because the oxidised products have been characterised only by their molecular weights and boiling points and the sulphones derived from petroleum thiophens have not been isolated[3,90,91].

Electrophilic substitution reactions are characteristic of thiophens, which is associated with the enhanced electron density in the α-position due to the presence of the sulphur atom. The sulphonation method has been used[92] for the isolation of a mixture of thiophens from petroleum distillates; the degree of their extraction did not exceed 45%.

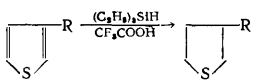
In reactions with bivalent mercury salts thiophens form organometallic derivatives:



However, the regeneration of thiophens from the mercurated products involves considerable losses[93]. The reaction has not therefore found extensive practical applications.

In a series of analytical studies[94–96] of middle and high-boiling distillates the method involving the dealkylation of thiophens free from other groups of OSC was used. It may be that the dealkylation reaction will be of practical importance for the analysis of fairly thoroughly purified concentrates of petroleum thiophens.

Ionic hydrogenation[97] with trifluoroacetic acid and triethylsilane can be used successfully to convert petroleum thiophens into the corresponding sulphides[97]:



The results of experiments on the hydrogenation of thiophen concentrates of different composition have shown that more severe conditions (a longer reaction time and a greater excess of trifluoroacetic acid) are required to attain a 70–86% degree of conversion of a mixture of thiophens than in the hydrogenation of individual thiophens[98]. The study of the structural-group composition of the products showed that the main compounds are monothiacycloalkanes and thiaindans; apparently derivatives of thiophens and benzothiophens were hydrogenated and in the case of the latter only the thiophen ring was hydrogenated.

Sulphuric acid concentrates of OSC obtained after the ionic hydrogenation reaction contain up to 70% of thiacycloalkanes and 20% of thiaindans, the overall sulphide content being 96%. Thus the application of the ionic hydrogenation method makes it possible to increase by 15–20% the content of sulphides in the sulphuric acid concentrates[23].

Since aromatic hydrocarbons (benzene, naphthalene, and their homologues) do not enter into the ionic hydrogenation reaction even under severe conditions, the method can be used to hydrogenate the thiophens in aromatic sulphur compound concentrates, particularly since they can be obtained (see Section II) on treatment with any solvents which extract aromatic hydrocarbons selectively. Further separation of the aromatic and organosulphur compounds can be achieved by sulphuric acid extraction[16,18]. Two products of practical importance can be obtained by this procedure: sulphide concentrates and aromatic hydrocarbons.

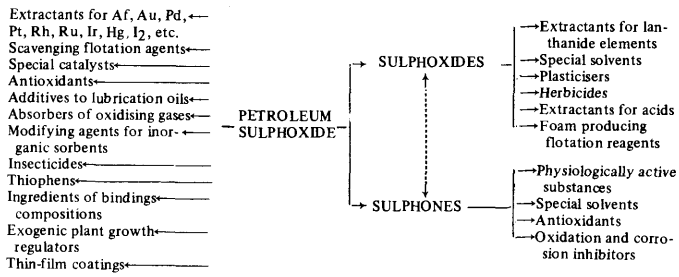


Figure 6. The applications of the sulphides in petroleum distillates; continuous arrows—tested on semi-industrial scale; dashed arrows—tested in the laboratory.

The ionic hydrogenation method is also promising for the conversion of thiophens directly in the distillates into the corresponding thiacycloalkanes, which are then extracted; this is particularly valuable in the study of the composition of the OSC in high-boiling petroleum distillates.

V. THE USE OF ORGANOSULPHUR COMPOUNDS OF PETROLEUM IN THE NATIONAL ECONOMY

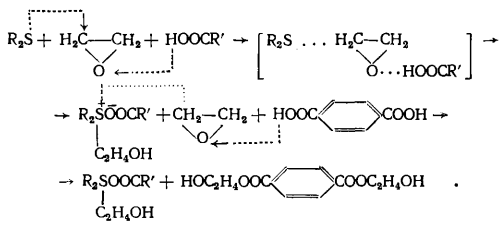
Studies of the compositions and properties of petroleum sulphides led to the discovery of their practical applications; in many instances large-scale industrial tests have been made (Fig.6). The oxidation of petroleum sulphides to sulphoxides and sulphones is of great practical importance; the preparation and properties of the latter have been examined in detail in a review[79]. It has been shown that sulphoxides can find extensive applications in hydrometallurgy and non-ferrous metallurgy as extractants and flotation agents. Studies in recent years have established that sulphoxides can be employed also in the chemical and petrochemical industry as effective solvents for phenols, resorcinol, catechol, hydroquinone[99], aromatic hydrocarbons[100], and acid oxides (SO_2, NO_2) contained in the waste gases released into the environment[101], and also as the starting materials for the synthesis of sulphones.

An extraction method has been developed for the elimination of monochloroacetic acid from sulphuric[102] and acetic[103] acids with the aid of sulphoxides. Sulphoxides have been tested successfully for the extraction of lower monocarboxylic acids from sewage[104] and of sulphur dioxide from industrial waste released into the atmosphere[105].

Some of the direct applications of petroleum sulphides are examined below.

1. Sulphides as Catalysts of the Oxidation of Terephthalic Acid

Individual OSC, for example thiacyclohexane[106], are known to be effective catalysts of the hydroxyethylation of terephthalic acid.



It has been shown[107] that petroleum OSC as well as thiacyclohexane are converted into a sulphonium salt by reaction with epoxyethane and terephthalic acid. The active complex obtained exhibits a high selectivity in the formation of bis-β-hydroxyethyl terephthalate.

OSC concentrates and purified sulphides isolated from petroleum distillates have been tested[23]. It has been found that an increase of the concentration of sulphide sulphur from 10.6 to 22.4% has a significant effect on the catalytic activity of sulphide concentrates, which is associated with the decrease of their content of thiophen derivatives. It has been noted that it is useful to obtain the sulphonium salts beforehand from OSC concentrates, epoxyethane, and terephthalic acid and then use them as catalysts.

A combined study has shown that the use of OSC concentrates (with $S_{sulph} \geq 20\%$) in the stage involving the hydroxyethylation of terephthalic acid makes it possible to obtain poly(ethylene terephthalate) with satisfactory physicomechanical parameters.

2. Petroleum Sulphides as Highly Effective Extractants for Noble Metals

The complex formation reaction between the sulphides and various metal salts is of enormous practical importance for the concentration and separation of silver[108,109] and platinum-group metals[29]. The results of studies on the extraction of silver by petroleum sulphides of different structure have been published[108] and a virtually quantitative isolation of silver of high purity has been achieved.

The extraction of platinum metals by petroleum sulphides in the presence of cumenyl and pentyl hydroperoxide has been investigated and it has been shown that all platinum metals are extracted from hydrochloric acid solutions (0.5 to 5.0 M) with a high partition coefficient[29]. The dependence of the rate of extraction of platinum metals on the nature of the diluent has been established. The possibility of the selective separation of a mixture of noble metals in the regeneration stage has been demonstrated[29].

3. Petroleum Sulphides as Effective Flotation Agents

The possibility of using petroleum sulphides as scavenging reagents and foaming agents in the flotation of copper-nickel and copper-molybdenum sulphide ores has been studied[110-112]. The scavenging and foam-forming properties of sulphides have been compared with those of reagents widely used in flotation such as potassium butylxanthate and the T-66 foaming agent. It has been shown that the scavenging capacity of the sulphides approaches that of the xanthate and their foam-forming capacity is greater than that of the T-66 foaming agent. The boiling points of the sulphide fractions, i.e. their molecular weights, have little influence on the results of flotation. A decrease of the foam-forming capacity of sulphides with increasing boiling point has been observed. It has been shown that the use of petroleum sulphides for the enrichment of polymetallic sulphide ores increases the degree of extraction of non-ferrous and noble metals and greatly reduces the cost of flotation agents.

4. Petroleum Sulphides as Exogenic Regulators of the Growth of Gramineous Plants

Studies have shown a high effectiveness of sulphides as a non-root feed for rye and wheat[113]. It follows from the experimental data that sulphides have a positive influence on the assimilation of nitrogen by plants and also promote a more intense formation of proteins. Spraying of spring wheat and winter rye with a solution of sulphides increases the crop and the quality of the grain as well as the yield of protein per hectare. Supplementary feeding with petroleum sulphides increases the crop of certain varieties of wheat by 13.5%.

5. OSC Concentrates as Binding Additives to Soils

Organosulphur compounds exhibit an effective adhesion and it is therefore of interest to test them as additives to soils. Between 0.9 and 1.1% of the OSC concentrate was added to a composition of binding substances consisting of crude petroleum and cement. The results of tests showed that, when the amount of binding material containing added OSC is 9.1–11.15% of the mass of dry soil, the stability of the latter increases by 30–50% and the water-stability coefficient increases by 11–15% compared with soils stabilised with petroleum containing added cement[114]. Thus dusty sands stabilised by the binding material have effective physicomechanical properties.

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In conclusion it must be emphasised that the study of the structural-group composition of the OSC of petroleum distillates is laborious and complicated. However, these investigations not only expand our ideas about the principal components of petroleums but, in combination with the development of industrial methods for their isolation, make it possible to create a scientific basis for the rational utilisation of the very rich store of organosulphur compounds which are of practical interest and are difficult to synthesise; they also permit the development, on the basis of studies of the chemical reactions of OSC, of methods of preparation of a wide variety of bifunctional and polyfunctional compounds of practical importance.

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Some Problems of the Kinetics of Radical Reactions in Solid Polymers

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The kinetics of radical reactions in solid polymers have a number of features which are examined in the present review in relation to the destruction of macroradicals, the reactions of macroradicals with macromolecules, and also the reactions involving low-molecular-weight substances. The mechanism and kinetics of the migration of the free valence in solid polymeric matrices are discussed in detail. Attention is concentrated on the relation between molecular mobility and the kinetics of radical reactions in solid polymers.
The bibliography includes 154 references.

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I. INTRODUCTION

Interest in theoretical problems of the kinetics of radical reactions in solid polymeric matrices arose in the period between the 1950's and 1960's in connection with the development of the radiation chemistry of polymers and later in connection with roblems of the stabilisation and modification of polymers and the micromechanics of their decomposition.

The first studies already showed that the kinetics of radical reactions in solid polymers are distinguished by a number of features: they depend to a greater extent than in the liquid phase on the physical properties of the medium, primarily on the molecular mobility; the main ideas about chemical kinetics, developed for reactions in the gas and liquid phases, namely the Law of Mass Action and the Arrhenius equation, in many instances do not hold formally, etc. This makes it necessary to regard the kinetics of radical reactions in solid polymers as an independent branch of chemical kinetics. The problems of the kinetics of radical processes in solid organic low-molecular-weight matrices are related to this field. The results of these studies have been surveyed in a series of reviews and monographs[1-11].

Unusual phenomena have been recently observed in this field, which entailed the creation of new theoretical models; the amount of quantitative kinetic information has increased. The aim of this review is to analyse the present state of the experimental and theoretical studies (primarily those of recent years) on the kinetics of radical reactions in solid polymers, to discover the main characteristics of these processes, and to formulate the main ideas and key problems. At the same time the review does not claim to cover fully the extensive experimental and theoretical data available.

II. KINETICS OF RADICAL REACTIONS IN SOLID POLYMERS

The kinetics of radical reactions in solid polymers are distinguished by a number of phenomenological features.

1. The transition from the liquid phase to solid polymers is frequently accompanied by the replacement of simple kinetic laws by complex laws specific to the solid phase. The most striking example is provided by the so-called stepwise kinetics—the decrease of the reaction rate long before the complete consumption of the reactants ("kinetic arrest"). It is observed in the recombination of radicals and radical pairs, in the addition of oxygen to macroradicals, in radical substitution, etc. The theory of stepwise kinetics has been described[2,10-13]. It is assumed that the observation of stepwise kinetics shows that the reacting species have a range of rate constants†. Therefore, in contrast to the usual kinetics, describing the reaction with the aid of a single "monchromatic" constant, the stepwise kinetics are frequently also referred to as "polychromatic".

2. In most cases the experimental Arrhenius parameters of the rate constants for bimolecular reactions in solid polymers (the effective activation energies and pre-exponential factors) are much higher than the "normal" values characteristic of gas-phase and liquid-phase reactions; they are frequently linked by the compensation relation [the compensation effect (CEF)]:

$$\lg (k_0)_{\text{eff}} = a + bE_{\text{eff}} \quad . \qquad (1)$$

The CEF is common in both chemical kinetics and in the kinetics of certain physical processes (diffusion, viscous flow, molecular mobility, etc.) and has been discussed in a number of studies[1,7,14-18]. In the vast majority of cases the CEF does not have a real physical significance and is merely a consequence of the incorrect application of the Arrhenius equation. The most general idea concerning the origin of the CEF has been put forward by Lebedev et al.[15] If the true activation energy varies with temperature for any reason, then the Arrhenius equation is strictly speaking inapplicable to the analysis of experimental results. However, if the temperature variation of the activation energy ($\partial E/\partial T$) is not too great, then the experimental data can be described formally by the Arrhenius equation within a comparatively narrow temperature range, but the effective values of E_{eff} and $(k_0)_{\text{eff}}$ then obtained differ from the true values:

$$E_{\text{eff}} = E - T(\partial E/\partial T) \quad ,$$
$$(k_0)_{\text{eff}} = k_0 \exp\left(-\frac{1}{R}\frac{\partial E}{\partial T}\right) \quad ,$$

and are linked by the compensation relation (1). If, for example, E = 10 kcal mol^{-1} and $\partial E/\partial T = -0.05$ kcal mol^{-1} K^{-1}, then at 300 K we obtain E_{eff} = 25 kcal mol^{-1}, i.e. 2.5 times greater than the true value. This is compensated by the apparent increase of the pre-exponential factor by a factor of 10^{11}.

†A recent study of the kinetics of the reaction $\dot{C}_2H_5 + O_2 \rightarrow C_2H_5\dot{O}_2$ in solid methanol[14] has shown that this conclusion is not ambiguous. If the stepwise kinetics are due to a range of rate constants, then the decrease of the concentration of $\dot{C}_2H_5$ can be described by the expression

$$[\dot{C}_2H_5] = [\dot{C}_2H_5]_0 \sum g_i \exp(-k_i[O_2]t) \quad ,$$

where g_i is the statistical weight of the rate constant k_i. The $\lg\{[\dot{C}_2H_5]/[C_2H_5]_0\} - [O_2]_t$ kinetic curves obtained for different values of $[O_2]\{[O_2] \gg [C_2H_5]_0\}$ should merge, which is not observed.

Another cause of the appearance of the CEF may be associated with the "polychromaticity" of the reaction kinetics in the solid phase. If the presence of a range of rate constants for the reacting species is caused by the presence of the corresponding range of activation energies, then the compensation effect automatically arises[16,17]. One must note that the CEF can obtain also for a fairly narrow range of rate constants when the "stepwise nature" of the kinetics is not yet observed directly.

3. The absolute values of the rate constants for reactions in solid polymers are in most cases much lower than the rate constants for the analogous reactions in the gas and liquid phases. This applies not only to rapid reactions, whose rates are limited in polymeric matrices by the rate of encounters of the reactants (this is quite natural), but also to the comparatively slow processes occurring under kinetic conditions.

4. As shown below, the kinetics of reactions in solid polymers are associated with the kinetics of molecular movement. In principle, there are two "channels" via which the molecular dynamics of the polymer can influence the kinetics of chemical reactions: (1) the change in the rate constant for the encounters as a result of a change in the coefficients of the translational diffusion of low-molecular-weight reactants as well as macroradicals and macromolecules (in the latter case as a consequence of the change in the frequencies and amplitudes of segmental movements); (2) the influence on the interaction of reacting species in the vapour and in the cage, i.e. on the chemical step proper. The first "channel", transmitting the influence of molecular mobility on the kinetics, is fairly trivial. On the other hand, the direct influence of molecular mobility on the chemical step is of great interest—it is specific to reactions in solid polymers and so far has no analogy in the liquid phase.

Apart from the fundamental characteristics of the kinetics of reactions in solid polymers indicated above, one may also mention a series of other less significant features—the clear kinetic non-equivalence of different regions of the polymer and the non-uniformity of the distribution of the reactants in the specimen (particularly in amorphous-crystalline polymers), which is frequently encountered. These anomalies are associated mainly with the structural-physical inhomogeneity (microheterophase nature) of many polymers and a fairly extensive "freezing" of the diffusion of the reacting species.

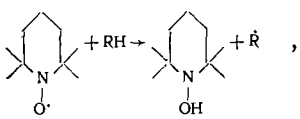
With increase of temperature, the intensity of molecular movement in the polymer increases, while at the same time the typical "solid-phase" stepwise kinetics approach increasingly closely the usual "liquid phase" kinetics. The glass point T_g constitutes the boundary, although the latter is not always sharp. On transition through T_g, a change in the kinetic laws governing the destruction of macroradicals[10], the isomerisation of low-molecular-weight substances in polymeric matrices[19-21], and complex processes such as oxidation[22] and graft polymerisation[23], is observed; there is also a change in the nature of the influence of the external pressure on the kinetics of the recombination of macroradicals[22-25]. At the temperature T_g a break is sometimes observed in the curves for the temperature variation of the rate of decomposition of radical initiators[26] and for the destruction of macroradicals[27,28], as well as for the diffusion coefficients of gases and vapours[29].

The stepwise solid-phase kinetics, which obtain under the conditions where molecular movements are extensively frozen below T_g, have been frequently discussed[1-4,10-13]. On the other hand, the kinetics of reactions in "softer" polymeric matrices, which are of great practical interest, have begun

to be studied extensively only in recent years. In the present review attention will be concentrated on the latter case.

Before considering the kinetics of specific radical reactions in solid polymers, it is necessary to answer the question whether the above kinetic anomalies are due to the high molecular weight of the reacting species or whether they are associated with the phase state of the polymer as a solid. Many factors support the second hypothesis.

1. The rate constants for the reactions of a stable nitroxy-radical, i.e.



with fused polyethylene and its low-temperature analogues (n-heptane and n-hexadecane) are identical at 175–220 °C.[30]

2. The rate constants for the reactions of the t-butoxy-radical with polypropylene, polystyrene, and their low-molecular-weight analogues in solution at 125 °C also hardly differ[31]. At a low temperature (45 °C) certain differences do appear, but they are probably caused by the presence under these conditions of a specific conformation of the macromolecules (coil) which decreases the accessibility of many sections of the macromolecules and is equivalent to a decrease of the effective concentration of the polymer.

3. The rate constants for the destruction of peroxy-macroradicals of polystyrene in solution at 25 °C (1.6×10^5 litre mol^{-1} s^{-1} [32]) and their low-molecular-weight analogues—the peroxy-radicals derived from isopropyl-benzene (10^4–10^5 litre mol^{-1} s^{-1} [33,34])—are very similar.

On the other hand, many kinetic features of the radical reactions in solid polymers are observed also in those cases where both reactants are low-molecular-weight substances (see Section III below) and also for reactions in solid low-molecular-weight matrices[1–3,8]. Thus the main cause of the kinetic anomalies of reactions in solid polymeric matrices is associated with the characteristics of the phase state of the above systems, mainly with the restriction of the molecular movement.

III. REACTIONS INVOLVING LOW-MOLECULAR-WEIGHT SUBSTANCES

The characteristic features of these reactions consist in the fact that at least one of the reactants migrates comparatively readily in the polymer via physical diffusion and the rate of the process is limited by the encounters of the reactants only for fairly rapid reactions. However, since the diffusion coefficients of low-molecular-weight substances in solid polymers are nevertheless lower than in liquids, the boundary at which the kinetics change to the diffusion-dependent type shifts to the region of slower reactions. For the majority of processes involving low-molecular-weight substances, the problem of their chemical nature does not arise and the kinetic information obtained can be referred to a specific elementary reaction.

The theory of diffusion-controlled reactions in solid matrices (including polymeric matrices) has been considered in a number of studies[2,7,10,35,36] and in the most general form by Whaite[37]. For a bimolecular reaction between A and B, where B is a low-molecular-weight substance, it is possible to distinguish three stages:

(1) the macrodiffusional stage in which the reactants are non-uniformly distributed in the given volume and B diffuses as a consequence of its concentration gradient;

(2) the microdiffusional stage—there is no concentration gradient and the rate of the process is determined by the rate of encounters of A and B, the encounters resulting in the formation of the pair [A...B];

(3) the kinetic stage—chemical interaction in the pair.

The case where there is no concentration gradient is of greater interest. According to the simplest model[35], chemical interaction takes place when A and B enter a single cage with a volume v^* (of the order of magnitude of the molecular volume). In the quasi-stationary approximation, we obtain the following expression for the concentration of the pairs [A...B]:

$$-d[A]/dt = -d[B]/dt = k_{eff}[A][B] \quad ,$$

$$k_{eff} = \frac{k_d k_x}{k_d + k_x} v^* \quad , \qquad (2)$$

where k_d and k_x are the rate constants for the microdiffusional and chemical stages. If $k_d \ll k_x$, then $k_{eff} \cong k_d v^*$ (stage 2 is rate-limiting); on the other hand, if $k_d \gg k_x$, then $k_{eff} \cong k_x v^*$ (stage 3 is rate-limiting). In the general case k_d and k_x are combined in accordance with the law of kinetic resistances [Eqn.(2)].

Although there are extensive experimental data on reactions with participation of low-molecular-weight substances, a large proportion of these are either qualitative or the kinetics have been studied under specific conditions (mechanodegradation, low temperature#), which preclude a sufficiently rigorous comparison of the rate constants obtained with the corresponding parameters of the liquid-phase reactions.

Fairly numerous studies have been made on the addition of oxygen to macroradicals. This process is of interest for the kinetics of the oxidation of polymers. The rate constants for the interaction of O_3 with alkyl radicals in the liquid phase are large (~10^8 litre mol^{-1} s^{-1} [33]) and therefore in solid polymers, where the diffusion coefficients of O_2 are significantly lower than in a liquid, this reaction usually proceeds under diffusion-dependent conditions[36,40–42]. Thus in polystyrene the rate of addition of O_2 is independent of the nature of the radicals[40]. The diffusion coefficients of O_2, obtained on the basis of the kinetics of the reaction $\dot{R} + O_2 \rightarrow R\dot{O}_2$, are close to the values found by independent methods. For example, D_{O_2}, obtained on the basis of the kinetics of the oxidation of allyl macroradicals in the amorphous phase of γ-irradiated polyethylene, is 1×10^{-10} cm^2 s^{-1} at 190 K,[41] while direct measurements of D_{O_2} [43] yielded 5×10^{-11} cm^{-2} s^{-1} (extrapolation to 190 K). The stepwise kinetics of the oxidation of macroradicals are observed at low temperatures[40,42], which agrees with the "stepwise" nature of the diffusion of oxygen itself[44]. However, according to Bresler and Kazbekov's data[3], the interaction of O_2 with the macroradicals of poly(methyl methacrylate), polystyrene, and poly(vinylacetate), obtained in the mechanodegradation of polymers, takes place under kinetic conditions and the observed rate constants are clearly lower than the diffusion-dependent values.

#At low temperatures tunnel effects can be significant[38,39].

Table 1. The rate constants for the reactions of low-molecular-weight substances in solid polymers and in the liquid phase (at 25 °C).

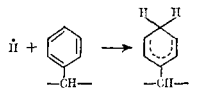
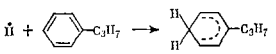
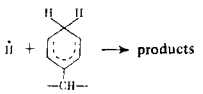
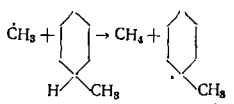
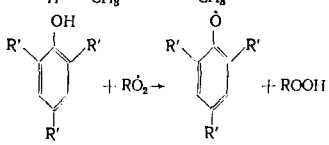
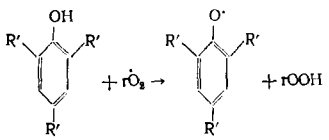
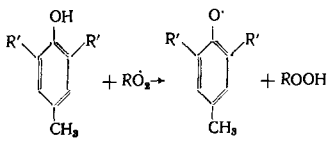
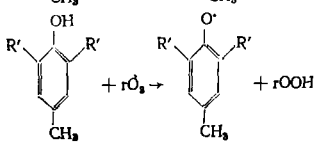
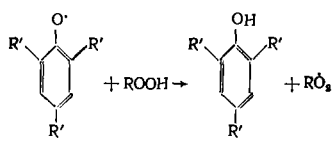
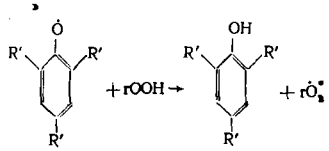
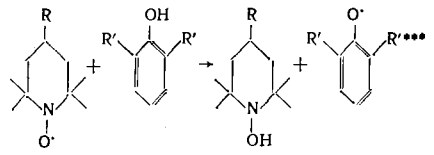
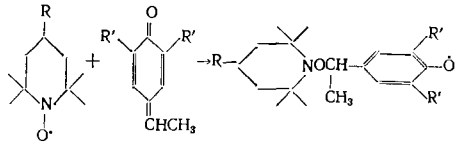
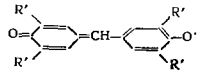
Reaction	Polymer or solvent	k_0, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k, litre mol^{-1} s^{-1}	References
	polystyrene	$0.4\cdot10^4$	1,3	$1\cdot10^4$	[48]
	n-heptane	—	—	$3.3\cdot10^8$(23°)	[33]
	polystyrene	$1.2\cdot10^6$	0.8	$3.2\cdot10^5$	[48]
$\dot{H}$ + radicals → products	liquid phase	—	—	$>10^8$	[33]
$\dot{C}H_3+RH\rightarrow CH_4+\dot{R}$	polypropylene	$2.7\cdot10^{11}$	20 6	0.2(100°)	[49]
	n-heptane	$7\,3\cdot10^9$	10.7	$3.8\cdot10^3$(100°)	[33]
	polypropylene	$6.3\cdot10^{15}$	19.8	$3.2\cdot10^3$(80°)	[46]
	ethylbenzene	$8\,8\cdot10^6$	4.1	$2.5\cdot10^4$(80°)	[50]
	polypropylene	—	—	$8.1\cdot10^3$(115°)	[51]
	ethylbenzene	$3.7\cdot10^7$	4.9	$6.5\cdot10^4$(115°)	[50]
	polypropylene	$2,5\cdot10^9$	16,0	$4,5\cdot10^{-3}$	[52]
ditto	polypropylene	$9,7\cdot10^{15}$	26,6	$3,1\cdot10^{-4}$	[46]
	polyethylene	$2,5\cdot10^{10}$	16,5	$2\cdot10^{-3}$	[52]
	benzene	$3,3\cdot10^6$	9,6	0,30	[45]

Table 1 (cont'd).

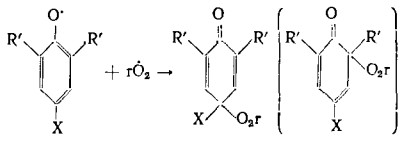
Reaction	Polymer or solvent	k_0, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k, litre mol^{-1} s^{-1}	References
$\dot{G} + ROOH \rightarrow RO_2\dot{} + GH$ **	polypropylene	$1{,}7 \cdot 10^{11}$	23,5	$1{,}1 \cdot 10^{-4}$	[53]
ditto	solution of polypropylene hydroperoxide in benzene	$1{,}6 \cdot 10^{5}$	10,0	$6{,}8 \cdot 10^{-3}$	[54]
	polypropylene	$5 \cdot 10^{8}$	18,0	$3 \cdot 10^{-5}$	[55]
ditto	benzene	$1{,}3 \cdot 10^{4}$	10.0	$5.6 \cdot 10^{-4}$	[55]
	polypropylene	$1.6 \cdot 10^{4}$	11.0	$1.4 \cdot 10^{-4}$	[56]
	benzene	$1.6 \cdot 10^{2}$	7.0	$1.2 \cdot 10^{-3}$	[56]

*Reaction with t-butyl hydroperoxide.

**$\dot{G}$ = galvinoxyl 

***R = $-COC_6H_5$.

Under diffusional conditions, the phenoxy-radicals apparently recombine with the macroradicals. In the liquid phase the rate constants for the reaction



(here and henceforth R′ = t-Bu in structural formulae) are close to 10^8 litre mol^{-1} s^{-1};[45] in solid polypropylene this quantity is significantly reduced: $k = 6 \times 10^6$ litre mol^{-1} s^{-1} for X = $C(CH_3)_3$ at 80 °C.[46] The diffusion coefficient of the 2,4,6-tri-t-butylphenoxy-radical estimated from these data (2.5×10^{-8} cm^2 s^{-1} at 80 °C) agrees with the diffusion coefficient of ionol, which has a similar molecular weight, measured directly in this polymer[47].

The reactions occurring under kinetic conditions are of much greater interest for the theory of radical reactions in solid polymers (Table 1). The data presented in Table 1 must be treated with extremely great caution. One of the reasons for this is that one cannot always eliminate from the polymer the residual amount of the solvents usually employed for the introduction of low-molecular-weight substances into the polymer. As will be shown below, sometimes even traces of the solvent are capable of greatly increasing the rates of reaction in solid polymers. For this reason, the measured rate constants[52,53,55,56] must be regarded as merely the upper limits of the true rate constants in solid polymeric matrices.

The first feature to which attention is drawn in the analysis of the data in Table 1 is a significant decrease (by a factor up to ~10^4) of the rate constants for reactions in solid polymers compared with the liquid phase. In most cases this is caused by the increase of the activation energy (the CEF is then usually observed); on the other hand, for reactions of hydrogen atoms, this is caused by the decrease of the pre-exponential factor§. We emphasise yet again that the decrease of the rate constants on transition to solid polymers, noted above, is in no way associated with diffusion-dependent obstacles—in certain cases (for example, in reactions of the methyl radical with polymers, of phenoxy-radicals with polymeric hydroperoxides, and of nitroxy-radicals with phenols) the rate constants for the encounters of the reactants, estimated from the diffusion coefficients of the corresponding low-molecular-weight substances exceed the experimental constants by 5–10 orders of magnitude.

Another characteristic feature of reactions involving low-molecular-weight substances, which was first observed by Karpukhin et al.[57], is some levelling of the reactivities of reactants having similar structures. Thus the rate constants for the reactions of peroxy-macroradicals with oxidation inhibitors (phenols, aromatic amines) in the solid polymers differ much less than in the liquid phase[46,50,57,59]. This phenomenon can hardly be explained by the fact that the above reactions proceed under diffusional conditions. This is particularly evident for reactions in the comparatively "soft" polypropylene at high temperatures, where the calculated rate constants for the encounters of the inhibitors with peroxy-radicals exceed the experimental reaction rate constants by a factor of 10^2–10^3.

§We may note that the rate constants for the reactions of hydrogen atoms have been measured at a low temperature where the tunnel mechanism frequently operates[38,39] and low pre-exponential factors are in fact characteristic of the tunnel mechanism.

The influence of molecular mobility on the rates of reactions involving low-molecular-weight radicals is extremely interesting. The rate constants for the reactions of phenoxy-radicals with polyolefin hydroperoxides[52,53] and of the nitroxy-radical with phenolic compounds[55] and methylenequinone[56] increase appreciably (the pre-exponential factors and activation energies diminish) after the addition of small amounts of chemically inert aromatic solvents and gradually approach the "liquid-phase" values (Table 2). The role of solvents, plasticising the polymer, evidently reduces to increasing the molecular mobility. Indeed the increase of the rate constants is correlated with the increase of the rotational frequency of the paramagnetic probe[52,55,56], characterising the intensity of the segmental movements in the polymer (Fig. 1). Since the above reactions are known to occur under kinetic conditions, one must consider the influence of molecular mobility directly on the chemical step. Presumably the decrease of the rate constants for the other reactions in Table 1, on passing from the liquid phase to the solid polymer, is also associated mainly with the decrease of molecular mobility.

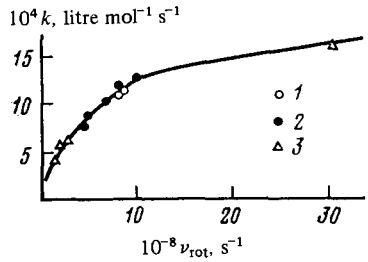


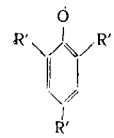
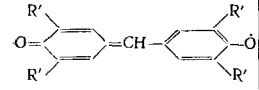
Figure 1. Dependence of the rate constant for the reaction of the 4-benzoyl-2,2,6,6-tetramethylpiperidinyloxy-radical with 2,4-di-t-butylphenol at 60 °C in polymer matrices [*1*) polyethylene; *2*) polypropylene; *3*) polystyrene] on the rotation frequency of the nitroxy-radical ν_{rot} (according to the data of Griva et al.[55]).

IV. DESTRUCTION OF MACRORADICALS

Although the number of studies devoted to the kinetics of the destruction of radicals in solid polymers is very large (they have been surveyed in a number of reviews[4,6-8,10-12]), only comparatively few of them define sufficiently clearly the experimental conditions: the nature of the radicals, their location and spatial distribution (the latter is particularly significant when the radicals are generated by ionising radiation), the concentration of low-molecular-weight substances, which can significantly influence the kinetics of the destruction process, as will be shown below, etc. We were therefore forced to approach very cautiously the discussion of the extensive experimental data, preference being given to studies in which the experimental conditions have been defined sufficiently unambiguously.

At temperatures below T_g the rate of destruction of radicals is usually low and is frequently described by stepwise kinetics. Above T_g, the usual bimolecular kinetics are as a rule observed¶, but the rate constants for the destruction of microradicals (k_t) are almost always lower than the corresponding constants in the liquid phase†, the effective activation energies are high, sometimes reaching 30–40 kcal mol^{-1}, and the CEF is usually observed. The kinetics of the destruction process are strongly influenced by factors which alter the intensity of the molecular movements in the polymer–orientation, mechanical deformation, external pressure, plasticisation, etc. (for further details, see below).

Table 2. The influence of benzene on the rate constants for the reactions of phenoxy-radicals with polypropylene hydroperoxide at 25 °C.

Phenoxy-radical	$[C_6H_6]$, %	k_0, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k, litre mol^{-1}	References
	0	$9.7\cdot10^{15}$	26.6	$3.1\cdot10^{-4}$	[46]
	≤0.4	$2.5\cdot10^{9}$	16.0	$3.5\cdot10^{-3}$	[52]
	8	$6.3\cdot10^{7}$	12.5	$3.8\cdot10^{-2}$	[52]
	100	$3.3\cdot10^{6}$	9.6	0.30	[45]*
	0	$1.7\cdot10^{11}$	23.5	$1.1\cdot10^{-4}$	[53]
	10	$5.2\cdot10^{4}$	9.5	$5.5\cdot10^{-3}$	[53]
	100	$1.6\cdot10^{5}$	10.0	$6.8\cdot10^{-3}$	[54]

*For the reaction with t-butyl hydroperoxide.

In solid polymers the rate of destruction of macroradicals is usually limited by the rate of their encounters and the problem of the kinetics of the destruction process thus reduces to the problem of the mechanism and kinetics of the processes leading to the encounters. For this reason, the study of the destruction of macroradicals yields information about the physical and chemical processes resulting in the migration of the free valence in the solid polymer rather than about the nature of the elementary step. One can imagine two fundamental mechanisms of such migration—physical diffusion of macroradicals and chemical migration of the free valence (relay process, "chemical" diffusion), which takes place as a result of the alternation of chemical reactions.

The rate constant k_e for the encounter of the radicals $\dot{R}_A$ and $\dot{R}_B$ is related to their diffusion coefficients (physical or "chemical" diffusion) D_A and D_B (cm^2 s^{-1}) by the

¶Faster initial sections are frequently noted, which is characteristic of diffusion-controlled processes[10,37].

†In the liquid phase the recombination (disproportionation) rate constants are usually 10^8–10^9 litre mol^{-1} s^{-1}, while the activation energies are close to zero. Peroxy-radicals are an exception; the rate constants for their destruction are significantly lower, particularly for tertiary peroxy-radicals (10^3–10^5 litre mol^{-1} s^{-1}, activation energies up to 8–10 kcal mol^{-1}).[33,59].

Smoluchowski equation:

$$k_e = 4\pi a(D_A + D_B)6\cdot 10^{20} \quad \text{(litre mol}^{-1}\text{ s}^{-1}\text{)},$$

where a is the effective distance (cm) over which the radicals interact chemically. If $D_A = D_B = D$, then

$$k_e \simeq 1.5\cdot 10^{22} aD \quad \text{(litre mol}^{-1}\text{ s}^{-1}\text{)}.$$

In the chemical migration the physical significance of the quantity D depends on the specific migration mechanism (see below), but in any case D is an effective parameter characterising the rate of migration of the free valence. As in the liquid phase, the quantity a is close to the kinetic diameter of small molecules (3–5 Å)#. The possible mechanisms of the encounters are examined below.

1. Physical Diffusion

At temperatures above T_g the intensity of small-scale molecular movements in polymers is fairly high and does not differ in principle from that in viscous liquids. For example, the rotation of stable nitroxy-radicals (the paramagnetic probe), controlled by the low-amplitude movements of elements of the macromolecules, takes place at a frequency in excess of 10^9 s^{-1} in polypropylene and polyethylene at temperatures in excess of 60 °C.[71–73]. According to high-resolution neutron spectroscopic data[74], the hydrogen atoms in the C–H bonds in the amorphous phase of polyethylene execute random movements about the equilibrium position with an amplitude of 2.5 Å and a frequency of $5 \times 10^{12} \exp(-4500/RT)$ ($\sim 5 \times 10^9$ s^{-1} at 60 °C), which is close to the rotation frequency of the paramagnetic probe. However, with the exception of radical pairs, the average distance between the radicals almost always significantly exceeds 3–5 Å and movements with this amplitude cannot therefore by themselves ensure the encounter of the radicals.

The movements of segments of the macromolecules are characterised by a much greater amplitude (up to 30 Å), but the diffusion coefficients corresponding to this type of molecular mobility are usually fairly low even at temperatures above T_g. Thus $D \cong 10^{-21}$ cm^2 s^{-1} near T_g in polystyrene[65]. In the comparatively "soft" polyethylene at 60 °C (higher by 60–80 °C than T_g) we have $D \cong 10^{-18}$ cm^2 s^{-1},[60] which corresponds to a rate constant for the encounters (for a = 5 Å) $k_e \cong 10^{-3}$ litre mol^{-1} s^{-1}; on the other hand, the experimental value of k_t for the destruction of peroxy-radicals under the same conditions is greater by 7 orders of magnitude[61]. This constitutes a further reason why there is no point in considering the diffusional mechanism of the encounters of macroradicals in the crystalline phase or in the amorphous phase at temperatures T_g, because the intensity of the segmental movements is then negligible. One must note that in many instances of practical importance (for example, in the oxidation of polyolefins[75]) the average distance between the radicals amounts to hundreds of angstroms and their encounters cannot be ensured by physical diffusion alone even in principle.

#According to Butyagin[70], the quantity a reaches 75 Å in polymers. Such high values of a, which evidently have no physical significance, are apparently obtained as a result of the not entirely correct application of Waite's diffusional model[37] to the analysis of experimental data for the kinetics of the destruction of macroradicals.

The absence of a dependence of the rate of destruction of macroradicals on their nature is a virtually unambiguous criterion of the diffusional mechanism of the encounters. This case apparently obtains above T_g in isobutylene and in the ethylene–propene copolymer, where the rate constants for the destruction of alkyl and peroxy-radicals are similar and the frequencies of the diffusional jumps calculated from the kinetic data for the destruction process are of the same order of magnitude as the frequencies of the segmental movements determined by independent methods[10]. On the other hand, the rate constants for the destruction of macroradicals usually depend greatly on their nature (Table 3) and this phenomenon cannot be accounted for by a change in the probability of reaction on encounter, because the peroxy-radicals, for which the destruction rate constants in the liquid phase are significantly lower than for other active radicals, are in fact destroyed at the highest rate[33]. A diffusional mechanism of the encounters can be postulated for radicals with a low reactivity (for example, the allyl radicals in polyethylene[60]), whose chemical migration is unlikely.

Table 3. The rate constants for the destruction of certain macroradicals (at 60 °C).

Polymer	Radical	t, °C	$(k_t)_0$, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k_t, litre mol^{-1} s^{-1}	Refs.
PE**	allyl	60÷100	$1.6\cdot 10^{21}$	35.0***	$1.6\cdot 10^{-2}$	
PE**	$RO_2^{\cdot}$	−5÷+24	$1.4\cdot 10^{16}$	18.5	$1\cdot 10^4$	[61]
i-PP**	$RO_2^{\cdot}$	25÷102	$3.2\cdot 10^{21}$	28.5	$6\cdot 10^2$	[62]
i-PP****	$RO_2^{\cdot}$	50÷90	$5\cdot 10^{15}$	24.7	$4.5\cdot 10^{-3}$	[63]
a-PP	$RO_2^{\cdot}$	45÷63	$1.3\cdot 10^{11}$	13.0	$3.6\cdot 10^2$	[64]
PS	alkyl	40÷100	$1\cdot 10^{15}$	24.0	0.18	[65]
PS	$RO_2^{\cdot}$	−25÷+14	$1.4\cdot 10^{10}$	13.0*****	40	—
PS	$RO_2^{\cdot}$	−8÷+10	$1\cdot 10^{14}$	17.6	$2.5\cdot 10^2$	[66]
PMMA	$\sim CH_2\dot{C}(CH_3)COOCH_3$	−40÷100	$1.5\cdot 10^{17}$	29.0	$1.5\cdot 10^{-2}$	[65]
PMMA	$RO_2^{\cdot}$	5÷37	$2\cdot 10^{13}$	19.2*****	5	—
PMMA	$RO_2^{\cdot}$	−22÷15	$2.5\cdot 10^{12}$	17.0	18	[67]
Nylon-6	alkyl	−3÷47	$1.3\cdot 10^9$	12.0	16	[68]
Nylon-6	$RO_2^{\cdot}$	−40÷+25	$1.6\cdot 10^{14}$	14.6******	$3\cdot 10^3$	—
PVA	alkyl	20÷61	$1\cdot 10^{15}$	23.0	0.8	[65]
PVA	$RO_2^{\cdot}$	−17÷37	$2\cdot 10^{10}$	13.5*****	28	—
PIB	alkyl and $RO_2^{\cdot}$	−63÷−23	$1.9\cdot 10^{17}$	18.0	11(−30°)	[10]
EPC	alkyl and $RO_2^{\cdot}$	−63÷−23	$3\cdot 10^{21}$	22.0	46(−30°)	[10]

*PE = polyethylene; *i*-PP = isotactic polypropylene; *a*-PP = atactic polypropylene; PS = polystyrene; PMMA = poly(methyl methacrylate); PVA = poly(vinyl acetate); PIB = polyisobutylene; EPC = ethylene–propene copolymer.
**In the amorphous phase.
***Calculated from data of Wenn et al.[60]
****In the crystalline phase.
*****Calculated from data of Bresler et al.[65]
******Calculated from data of Davydov et al.[69]

Analysis of experimental data suggests that the diffusional mechanism of the destruction of macroradicals in solid polymers is more an exception than the rule, and that in most cases neither the amplitude nor the intensity of the molecular movements can ensure the encounter of the radicals. From the standpoint of the diffusional mechanism of the migration of the free valence, the acceleration of the destruction of macroradicals in the presence of low

concentrations of chemically active low-molecular-weight substances (H_2, O_2, Cl_2, cumenyl hydroperoxide, monomers, etc.) is completely inexplicable. There is no doubt that the main mechanism ensuring the encounter of macroradicals in solid polymers at not unduly high temperatures is "chemical" diffusion.

2. The Relay Migration of the Free Valence with Participation of Macroradicals Alone

This version of "chemical" diffusion has been most widely discussed in the literature. The migration of free valence can be achieved as a result of a sequence of identical-transfer reactions, for example, for alkyl radicals in polyethylene:

$$\sim CH_2\dot{C}HCH_2 \sim + \sim CH_2CH_2CH_2 \sim \rightarrow \sim CH_2CH_2CH_2 \sim + \sim CH_2\dot{C}HCH_2 \sim \quad (3)$$

or the repetition of a cycle of reactions, for example for the destruction of peroxy-radicals:

$$R\dot{O}_2 + RH \rightarrow \dot{R} + ROOH \quad , \quad (4)$$

$$\dot{R} + O_2 \xrightarrow{fast} R\dot{O}_2 \quad . \quad (5)$$

We shall refer to this type of migration mechanism as trivial relay; it has been proposed by Dole et al.[76] and Koritskii et al.[77] and subsequently developed[7,65,78]. The effective diffusion coefficient, characterising the trivial relay, is defined by the expression

$$D_r = \frac{\lambda_r^2 k_p [RH]}{6} \quad ,$$

where λ_r is the average distance over which the free valence migrates during a single "step" (of the order of magnitude of the length of a chemical bond), k_p is the rate constant for the rate-limiting reaction in the relay process [for example, reaction (3) or (4)] and [RH] is the concentration of the monomeric unit; the product k_p[RH] has the significance of the jump frequency. The rate constant for encounters is given by the following expression:

$$k_e = \frac{8\pi a \lambda_r^2 k_p [RH]}{6} 6 \cdot 10^{20} \simeq 2.5 \cdot 10^{21} a \lambda_r^2 k_p [RH] \text{ (litre mol}^{-1}\text{ s}^{-1}\text{)}. \quad (6)$$

The principal argument in support of the trivial relay is the sharp increase of the constant k_t in the series of radicals allyl < alkyl < peroxy,[8] in qualitative agreement with the variation of k_p in the same sequence[33].

The most significant experimental confirmation of this mechanism of the migration of the free valence is available for peroxy-radicals. The destruction of peroxy-macroradicals is accompanied by the chain process involving the absorption of O_2 and the formation of a hydroperoxide[7,79,80]. In fact the chain oxidation of polymers is itself a process involving the relay migration of the free valence.

Oxygen in many instances accelerates the destruction of alkyl macroradicals even when the concentration of peroxy-radicals is too low to be detected by EPR.[81-83]. This is possible if the rate of reaction (5) is comparatively low and the chain propagation reaction (4) is in fact very effective. Analysis of this situation shows[81,82] that the kinetics of the destruction of alkyl radicals should obey a bimolecular law and the effective rate constant should be proportional to the oxygen concentration, which agrees with experiments[81].

Comparison of the experimental values of k_t and k_e, calculated by Eqn.(6), is possible only in rare instances, since accurate values of the rate constant k_p in solid polymers, necessary for the calculation of k_e, are usually unknown.

Sufficiently reliable values of k_t and k_p are available for peroxy-radicals in amorphous atactic polypropylene[64] and in the amorphous phase of isotactic polypropylene[62,80,84]. It has been shown[62,85] that at 60 °C $k_t = 6 \times 10^2$ litre mol^{-1} s^{-1} and $k_p = 1.5 \times 10^{-2}$ litre mol^{-1} s^{-1}. Assuming that $\lambda_r = 3 \times 10^{-8}$ cm, $a = 5 \times 10^{-8}$ cm, and [RH] = 22 M, we find $k_e = 3.7 \times 10^{-2}$ litre mol^{-1} s^{-1} from Eqn.(6), i.e. lower by 4 orders of magnitude than the experimental value of k_t. A similar result has been obtained also for atactic polypropylene. In order to achieve agreement between k_e and k_t, it is necessary to assume that, under the given conditions, the "step" of the relay is $\lambda_r \cong 400$ Å, which is naturally unrealistic within the framework of the trivial relay.

An unusual version of the relay mechanism of the migration of the free valence obtains under the conditions of graft polymerisation. When the monomer M is brought into contact with a polymer containing stabilised macroradicals $\dot{R}_p$, a chain polymerisation process develops:

$$\dot{R}_p + M \rightarrow [\dot{R}_M]_1$$
$$\cdots\cdots\cdots$$
$$[R_M]_i + M \xrightarrow{k_{po}} [\dot{R}_M]_{i+1} \quad .$$

This process is accompanied by an appreciable acceleration of the destruction of macroradicals.

One chain propagation step leads to the migration of the free valence over a distance λ_{po}, equal to two chemical bond lengths (~2–3 Å); the jump frequency is evidently k_{po}[M]. Then the effective diffusion coefficient for the migration of the free valence is $D_{po} = \lambda_{po}^2 k_{po}$[M]/6 while the bimolecular rate constant for the encounters of the radicals is

$$k_e = 2.5 \cdot 10^{21} a \lambda_{po}^2 k_p [M] \quad .$$

This mechanism of the migration of the free valence is in essence similar to that of migration with participation of macroradicals alone. The difference is that the slow stage of the relay

$$\dot{R}\ (R\dot{O}_2) + RH \xrightarrow{k_p} RH\ (ROOH) + \dot{R}$$

is replaced by the much faster polymerisation chain propagation reaction. The ratio of the rate constants for the encounters determined by chain polymerisation and the trivial relay mechanism, which amounts to k_{po}[M]/k_p[RH], can be fairly large even for [M] << [RH], because the ratio k_{po}/k_p for vinyl monomers reaches 10^3–10^5.[33]

The results of the study of the kinetics of the destruction of macroradicals in the postpolymerisation of tetrafluoroethylene on γ-irradiated Teflon[87] agree satisfactorily with the analysis presented above.

3. The Relay-Diffusion Mechanism of the Migration of the Free Valence

As shown in the preceding section, the simplest variant of "chemical" diffusion—the trivial relay—is usually unsatisfactory. Firstly, the trivial relay does not explain the fairly large "step" in the relay, reaching sometimes hundreds of angstroms, and the high absolute rates of migration of the free valence observed in many cases. Secondly, in this variant of "chemical" diffusion, purely physical stages of the migration of the free valence are in essence ignored, which, as a rule, prevents a quantitative explanation of the clear relation between the kinetics of the destruction of radicals and molecular mobility. The idea that mobility influences the chemical step proper in the valence transfer reaction does not always help. The calculation of the rate constants for encounters by Eqn.(6), even

when "liquid-phase" rate constants for the transfer of valence k_p (which is apparently the upper limit of this quantity in solid polymers[88]) are used, leads to values of k_e which are in many instances lower by several orders of magnitude than the experimental k_t.

We shall consider the relay-diffusion model of the migration of the free valence in which the chemical relay is combined with the diffusional migration of segments (Fig.2). As an example, we shall consider reaction (3). As a result of the thermal movement of the segments, both the radical centre $-\dot{C}H-$ (black circle) and the $-CH_2-$reaction group (open circle) are capable of migrating within a sphere having a radius λ_s of the order of magnitude of the size of the segment. This single reaction step can result in the transfer of the free valence over a distance up to $2\lambda_s$. Depending on the ratio of the frequencies of segmental movements (ν_s) and relay transfer steps {k_p[RH]}, the followng extreme situations are possible. If $\lambda_s \ll k_p$[RH] (molecular mobility is greatly reduced), then the segmental movements should not contribute much to the migration process and this case will not differ from the trivial relay considered in the previous section. If the segmental mobility is high {$\nu_s \gg k_p$[RH]}, then during a period $1/k_p$[RH] between two elementary steps in the transfer of the free valence, the reaction centres have sufficient time to move around the entire sphere with a radius λ_s and during a single "step" of the relay the free valence migrates not over a distance λ_r but over a much larger distance in the range $\lambda_r < \overline{\lambda}_s \leq 2\lambda_s$. Thus the chemical relay takes place with a step close to the characteristic amplitude of the segmental movements. The analytical expression for the rate constant for encounters is analogous to the Eqn.(6), it being only necessary to replace λ_r by $\overline{\lambda}_s$. If the frequencies of the segmental movements and of the relay are comparable, then k_e has an intermediate value.

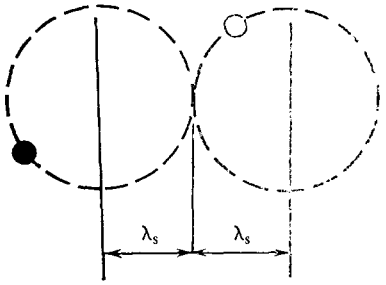


Figure 2. Illustration of the relay-diffusional model of the destruction of macroradicals in solid polymers.

It must be emphasised that in the mechanism of the transfer of the free valence considered here the decisive factor remains the chemical relay, the segmental mobility ensuring only a much larger step in the relay. The relay-diffusion mechanism agrees with the idea that diffusion-controlled stages are present in this process—the stages comprising the movements of the segments are of this kind. In very "rigid" polymers, where even a limited segmental mobility is virtually absent, the step of the relay is $\lambda \cong 1.5$–3 Å and the migration of valence is ensured solely by the chemical reaction (trivial relay). In "soft" polymers the amplitude of segmental movements is large ($\overline{\lambda}_s$ up to 60 Å), which, in principle, can ensure fairly high rates of migration.

Since the effective diffusion coefficient of the free valence is proportional to λ^2, even a comparatively small increase of the parameter λ leads to an appreciable increase in the rate of migration of the free valence compared with the trivial relay—in the limit by a factor $(2\lambda_s/\lambda_r)^2$. This can evidently still prove to be inadequate to explain the very rapid macroradical destruction processes. For example, in the case of the destruction of peroxy-radicals in polypropylene at 60 °C considered in the previous section {$k_p = 1.5 \times 10^{-2}$ litre mol^{-1} s^{-1}, [RH] = 22 M, $a = 5 \times 10^{-8}$ cm}, k_e is only 15 litre mol^{-1} s^{-1} even for $\lambda_r = 2\lambda_s = 60$ Å, which is lower by a factor of 40 than the experimental value $k_t = 6 \times 10^2$ litre mol^{-1} s^{-1}.

4. Migration of the Free Valence with Participation of Low-Molecular-Weight Radicals (Kinetic Analysis)

The constant k_e can increase sharply if low-molecular-weight radicals, with a much greater mobility than macroradicals and therefore capable of migrating over comparatively long distances in the solid polymer, participate in the migration processes. The analytical expressions for D_r and k_e depend on the mechanism of the formation of light radicals. We shall consider three versions: chain transfer to the low-molecular-weight admixture, the dissociation of macroradicals, and the formation of light radicals in the decomposition of the initiator.

The case of the transfer of the free valence to a low-molecular-weight admixture rH as a result of the reaction

$$\dot{R} + rH \xrightarrow{k_1} RH + \dot{r} \qquad (7)$$

has already been considered[89]. If $\dot{r}$ disappears mainly in the reverse free valence transfer reaction

$$\dot{r} + RH \xrightarrow{k_2} rH + \dot{R} \quad , \qquad (8)$$

then its lifetime between elementary steps of reactions (7) and (8) is $\tau = 1/k_2$[RH]. During the time τ, the radical $\dot{r}$ (its diffusion coefficient is D_0) makes a jump over a distance

$$\lambda = \sqrt{6D_0\tau} = \sqrt{6D_0/k_2[RH]}$$

and the frequency of these jumps is evidently $\nu = k_1$[RH]. For the effective diffusion coefficient of the free valence, one can write

$$D_r = \lambda^2\nu/6 = k_1D_0[rH]/k_2[RH] \quad .$$

The corresponding expression for the rate constant for encounters is

$$k_e = \frac{4\pi a 2D_0k_1[rH]}{k_2[RH]} 6 \cdot 10^{20} \simeq 1.5 \cdot 10^{22} \frac{aD_0k_1[rH]}{k_2[RH]} \quad . \qquad (9)$$

The derivation of Eqn.(9) can be approached in a different way. Since usually $[\dot{r}] \ll [\dot{R}]$, the reaction

$$\dot{r} + \dot{R} \xrightarrow{k_3} \text{products} \qquad (10)$$

can be regarded as virtually the only one in which the total number of radicals diminishes. The kinetic mechanism incorporating reactions (7), (8), and (10) is described by the system of differential equations

$$d[\dot{r}]/dt = k_1[\dot{R}][rH] - k_2[\dot{r}][RH] - k_3[\dot{r}][\dot{R}] \quad ,$$

$$d[\dot{R}]/dt = -k_1[\dot{R}][rH] + k_2[\dot{r}][RH] - k_3[\dot{r}][\dot{R}] \quad .$$

When the concentration of $\dot{R}$ is high and $k_3[\dot{R}] \gg k_2[RH]$, we obtain for the rate of destruction of macroradicals

$$-d[\dot{R}]/dt \simeq 2k_1[rH][\dot{R}] \ .$$

On the other hand, usually $k_3[\dot{R}] \ll k_2[RH]$, which implies that the encounter of the free valences is preceded by several cycles of reactions (7) and (8) or, in other words, the distance over which $\dot{r}$ migrates during its lifetime is significantly shorter than the overall migration path of the free valence before destruction. Then

$$-d[\dot{R}]/dt \simeq \frac{2k_1k_3[rH]}{k_2[RH]}[\dot{R}]^2 \ ,$$

i.e. the destruction of macroradicals is described by a second-order equation with respect to the radical with the effective constant

$$k_{eff} = 2k_1k_3[rH]/k_2[RH] \ . \qquad (11)$$

We shall assume that reaction (10) is controlled by diffusion with D_0, whereupon we obtain

$$k_3 = 4\pi aD_0 \times 6 \times 10^{20} \ . \qquad (12)$$

On substituting Eqn.(12) in Eqn.(11), we obtain Eqn.(9). If the low-molecular-weight radicals are formed in the dissociation of macroradicals or in the decomposition of the initiator Y, reaction (7) must be replaced by reactions (13) and (14) respectively:

$$R \xrightarrow{k_4} \dot{r} + \text{products} \quad ; \qquad (13)$$

$$Y \xrightarrow{w_0} \dot{r} \ . \qquad (14)$$

Table 4. Kinetics of the destruction of macroradicals as a result of the migration of the free valence with participation of light radicals.

No. of radical r formation reaction	Rate of destruction of macroradicals		k_e for $k_3[\dot{R}] \ll k_2[RH]$
	for $k_3[\dot{R}] \gg k_2[RH]$	for $k_3[\dot{R}] \ll k_2[RH]$	
(7)	$2k_1[rH][\dot{R}]$	$\frac{2k_1k_3[rH][\dot{R}]^2}{k_2[RH]}$	$1.5 \cdot 10^{20}\frac{aD_0k_1[rH]}{k_2[RH]}$ (9)
(13)	$2k_4[\dot{R}]$	$\frac{2k_3k_4[\dot{R}]^2}{k_2[RH]}$	$1.5 \cdot 10^{20}\frac{aD_0k_4}{k_2[RH]}$ (9a)
(14)	w_0	$-w_0$	—

The expressions for the rate of destruction of macroradicals and the rate constant for the encounter of the free valences, obtained in terms of an approximation analogous to that used in the previous case, are presented in Table 4.

The above analysis shows that the bimolecular law governing the destruction of macroradicals with participation of light radicals, which is most frequently observed experimentally, can be realised if the source of light radicals is reaction (7) or (13), while $k_3[\dot{R}] \ll k_2[RH]$. If, on the other hand, the low-molecular-weight radicals are formed in the decomposition of the initiator, then the bimolecular law governing the destruction of macroradicals should not be observed for any values of $[\dot{R}]$.

We shall compare the bimolecular rate constants for encounters in the migration of the free valence with participation of light radicals (k_{e_1}) and as a result of the trivial relay (k_{e_2}), having assumed that the distance a over which the radicals react chemically is in both cases the same. When $\dot{r}$ is formed via reactions (7), the ratio k_{e_1}/k_{e_2} can be obtained on dividing Eqn.(9) by Eqn.(6):

$$k_{e1}/k_{e2} = 6D_0k_1[rH]/\lambda_r^2k_2k_p[RH]^2 \ .$$

Assuming that $\lambda_r = 3 \times 10^{-8}$ cm, $k_2 = k_p = 10^{-1}$ litre mol^{-1} s^{-1}, [RH] = 10 M, and $D_0 = 10^{-10}$ cm^2 s^{-1}, we find $k_{e_1}/k_{e_2} \cong 7 \times 10^5k_1[rH]$. The ratio $k_{e_1}/k_{e_2} \gg 1$ holds subject to the condition that $k_1[rH] \gg 1.5 \times 10^{-6}$ s^{-1}, which obtains readily even for comparatively low values of [rH]. If $\dot{r}$ is formed in the dissociation of macroradicals, the ratio k_{e_1}/k_{e_2} is obtained on dividing Eqn.(9a) by Eqn.(6):

$$k_{e1}/k_{e2} = 6D_0k_4/\lambda_r^2k_2k_p[RH]^2 \ .$$

Using the same values of λ_r, k_2, $k_p[RH]$, and D_0 as in the previous case, we find that $k_{e_1}/k_{e_2} \gg 1$, provided that $k_4 \gg 1.5 \times 10^{-6}$ s^{-1}, which is frequently also readily obtainable.

Thus the involvement of light radicals can ensure a more effective migration of the free valence than the trivial relay and the relay-diffusional mechanism of migration. It is then possible to attain fairly high absolute values of k_e. For example, an estimate[89] for the destruction of peroxy-radicals in polypropylene undergoing oxidation at 130 °C, based on the assumption that the free valence is transferred to low-molecular-weight products of thermo-oxidative degradation, leads to $k_e \cong 10^5$–10^6 litre mol^{-1} s^{-1}, which is fairly close to the experimental values of k_t.[62,90] The mechanism of migration with participation of light radicals also agrees well with the idea that diffusion-controlled stages are present in the migration process; in the present instance the diffusion of light radicals is such a stage.

Table 4 shows that the two mechanisms of the formation of low-molecular-weight radicals [reaction (7) and (13)] cannot be distinguished solely on the basis of data for the kinetics of the destruction of macroradicals. The low-molecular-weight chain transferring agents rH in reaction (7) can be both specially introduced additives and random admixtures as well as polymer degradation products (in particular a high yield of low-molecular-weight products is observed in thermo-oxidative degradation). The latter case has been discussed[89].

We shall now consider a more universal mechanism of the formation of light radicals—the dissociation of macroradicals. Radicals tend to dissociate to a greater extent than the corresponding molecules, and the commonest dissociation mechanism involves the dissociation of the β-bond (the so-called β-decomposition). Radical recombination and disproportionation processes compete with the dissociation reaction. Since the lifetime τ_1 of active radicals in the liquid and gas phases is usually short and rarely exceeds 1 s, it is possible to observe only comparatively rapid dissociation processes under these conditions§. The situation changes in solid polymers where τ_1 is significantly greater and sometimes reaches many hours.

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§In the bimolecular mechanism of the destruction of radicals $\tau_1 = 1/\sqrt{w_0k_t}$; the usual value of k_t for active radicals in the liquid phase is 10^9 litre mol^{-1} s^{-1},[33] while the rate of initiation w_0 in kinetic experiments is rarely below 10^{-9} mol litre^{-1} s^{-1}. Hence $\tau_1 \leq 1$ s. The probability of the dissociation of the radical is 10% subject to the condition that $k_4 = 0.1/\tau_1 \geq 0.1$ s^{-1}; thus in the liquid phase it is virtually impossible to detect dissociation processes with $k_4 < 0.1$ s^{-1}.

One can therefore expect that macroradical dissociation processes play a considerably greater role than the analogous reactions of low-molecular-weight radicals in the liquid and gas phases¶.

5. Migration of the Free Valence with Participation of Low-Molecular-Weight Radicals (Experimental Data)

We shall now consider experimental facts indicating the involvement of light radicals in free valence migration processes in solid polymers.

1. When chlorine is brought into contact with γ-irradiated polyethylene containing stable alkyl radicals, the polymer undergoes chain chlorination, which is accompanied by a decrease of the concentration of macroradicals at a rate several orders of magnitude greater than in the absence of molecular chlorine[96]. The high rate of destruction of alkyl radicals is ensured by the participation in the migration process of $\dot{C}l$ atoms formed by the reaction

$$\dot{R} + Cl_2 \rightarrow RCl + \dot{C}l$$

and capable of traversing comparatively long distances before recombining with $\dot{R}$ or before the reverse chain transfer reaction step:

$$RH + \dot{C}l \rightarrow \dot{R} + HCl \quad .$$

In this case chlorine plays the role of a kind of catalyst of the destruction of macroradicals.

2. Catalysis of the migration of the free valence by hydrogen is observed in γ-irradiated polyethylene[97-100]. The rate of migration can be inferred from the kinetics of not only the destruction of alkyl radicals ($\dot{R}_{alk}$) but also of the conversion of $\dot{R}_{alk}$ into allyl radicals ($\dot{R}_{all}$) (the rate of the latter process is apparently limited by the rate of encounters of the free valence with a double bond). Both processes are significantly accelerated by hydrogen (by a factor of ~15 for p_{H_2} = 400 mmHg at 24 °C in the transition $\dot{R}_{alk} \rightarrow \dot{R}_{all}$) and to a lesser extent by deuterium, the magnitude of the effect being proportional to the H_2 of D_2 pressure.

In the absence of hydrogen, the migration of the free valence in the polymer apparently takes place as a result of the reaction

$$\dot{R}_{alk} + RH \xrightarrow{k_6} RH + \dot{R}_{alk} \quad . \qquad (15)$$

In a hydrogen atmosphere migration can take place as a consequence of the repetition of the reaction cycle:

$$\begin{aligned} &\dot{R}_{alk} + H_2 \xrightarrow{k_7} \dot{H} + RH \quad , \\ &\dot{H} + RH \rightarrow H_2 + \dot{R}_{alk.} \end{aligned} \qquad (16)$$

The occurrence of deuterium isotope exchange in such a system[97] confirms the above mechanism. Reaction (16) can be more effective than reaction (15) from the standpoint of the migration of the free valence in the polymer, although $k_7 \ll k_6$. This is associated with the exceptionally high mobility of H atoms†.

3. The rate of the chain oxidation of polyolefins decreases in the presence of the low-molecular-weight hydroperoxide $C_6H_5C(CH_3)_2OOH$.[102] The effect is evidently also caused by the increase of the effective termination rate constant as a result of the involvement in this process of light radicals arising in the reaction

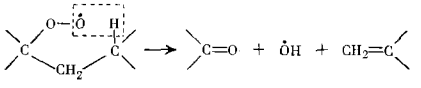
$$R\dot{O}_2 + C_6H_5C(CH_3)_2\dot{O}OH \rightarrow ROOH + C_6H_5C(CH_3)_2O\dot{O}.$$

This mechanism has been confirmed directly in a study[75] where the increase of the rate of destruction of peroxy-radicals in polypropylene in the presence of a low-molecular-weight hydroperoxide {by a factor of ~7 for $[C_6H_5C(CH_3)_2.OOH] = 0.12$ M at 25 °C} was observed directly by EPR. However, the effect is comparatively small, which implies that an extremely effective migration mechanism, possibly involving low-molecular-weight radicals (see below), obtains in solid polypropylene even without the addition of a low-molecular-weight hydroperoxide.

4. In poly(methyl methacrylate), polystyrene, and poly(vinyl acetate) at temperatures below T_g, i.e. under the conditions of highly limited mobility of the polymer molecules, the destruction of macroradicals proceeds at a measurable rate (Table 3) and is accompanied by the formation of considerable amounts of low-molecular-weight products[67,103]. The authors[67,103] concluded that the high rates of destruction of radicals are ensured by the involvement in the free valence migration processes of low-molecular-weight radicals arising on dissociation of the macroradicals. A new confirmation of this migration mechanism in polystyrene has been recently obtained[104]. The destruction of the peroxy-macroradicals in the presence of an alkyl radical acceptor—a stable nitroxy-radical $R_2\dot{N}O$—is accompanied by the formation of the ether R_2NOr, which is not "attached" to the polymer. This evidently implies that low-molecular-weight alkyl radicals arise in some way in processes leading to the destruction of macroradicals.

5. Light radicals apparently play a significant role also in processes involving the destruction of peroxy-macroradicals in polypropylene and polyethylene. The thermal oxidation of polyolefins is accompanied by the formation of volatile products[7] and of low-molecular-weight as well as polymeric hydroperoxides[105]. These data indicate an intense decomposition of the macroradicals, in which the decomposition products can include low-molecular-weight radicals. The latter have been detected directly by EPR in the thermal decomposition of solid polypropylene hydroperoxides[106]. It was assumed earlier that the dissociation is undergone mainly by alkoxy- and terminal alkyl radicals. However, recent studies have shown that one of the main processes responsible for the degradation of polyethylene[107] and polypropylene[108,109] is the decomposition of peroxy-macroradicals#.

A specific mechanism of the decomposition of RO_2 has been proposed[112,113]:

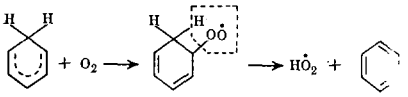


¶This also applies to low-molecular-weight sterically hindered radicals, which cannot compete or disproportionate with one another even in the liquid phase owing to steric hindrance. The range of such radicals has greatly expanded in recent years[91-95]. Many of these are destroyed at a low rate as a result of the β-decomposition followed by the recombination of the fragment radical with the initial radical.

†In solid polymers hydrogen atoms diffuse over distances up to ~10^{-6} cm without reacting with macroradicals[101].

#Data indicating the dissociation of peroxy-radicals in polytetrafluoroethylene have been published[22,110,111].

However, the ȮH radicals formed in this process are very reactive and for this reason can hardly traverse long distances in the polymer. Another mechanism of the decomposition of $\dot{R}O_2$ can be associated with the ejection of the considerably less active $H\dot{O}_2$ radical. Processes of this kind are known in the liquid phase close to room temperature for peroxy-radicals derived from hydroxy-compounds[114,115] and certain unsaturated hydrocarbons[116], for example, in the oxidation of cyclohexa-1,4-diene:



This mechanism has been invoked to account for the sharp increase of the rate of destruction of macroradicals of the cyclohexadienyl type in polycarbonate in the presence of O_2.[117] One cannot rule out the possibility that the decomposition of $R\dot{O}_2$ with ejection of $H\dot{O}_2$ takes place also in polyolefins and other polymers.

The bimolecular rate constant for the destruction of peroxy-radicals in polypropylene subjected to preliminary oxidation decreases with increase of the concentration of the polymeric hydroperoxide in accordance with the law[75,80]

$$k_t = \frac{a}{b + c[\mathrm{ROOH}]} \quad , \qquad (17)$$

where a, b, and c are constants. This dependence of k_t on [ROOH] can be accounted for most naturally within the framework of the mechanism of migration with participation of low-molecular-weight radicals. The polymeric hydroperoxide plays in this case the role of a trap for light radicals. As a result of the reaction

$$\dot{r} + \mathrm{ROOH} \xrightarrow{k_1} rH + R\dot{O}_2 \quad ,$$

the latter are replaced by polymeric peroxy-radicals, which reduces the effective rate of migration. The expression for the rate constants for the encounters of the free valences will differ from those quoted in Table 4 by the fact that the term k_1[ROOH] appears in the denominator. For example, if the light radicals arise in the dissociation of the macroradical $R\dot{O}_2$, the following expression is obtained:

$$k_e = 1{,}5 \cdot 10^{28} \frac{aD_0 k_t}{k_2[\mathrm{RH}] + k_1[\mathrm{ROOH}]} \quad ,$$

the form of which does not differ from that of Eqn.(17). Of the two possible mechanisms of the formation of light radicals participating in the migration of the free valence—chain transfer to a low-molecular-weight impurity and the dissociation of the macroradical—the second mechanism is more probable in the given instance[75].

6. The Influence of Molecular Mobility on the Kinetics of the Destruction of Macroradicals

Many facts are known indicating a relation between the kinetics of the destruction of macroradicals in solid polymers and molecular mobility—the decrease of the rate of destruction on passing from an amorphous to a crystalline phase[8,15,63,118–119], a lower value of k_t in oriented specimens compared with non-oriented specimens[65,120], the increase under these conditions of the effective activation energy for the destruction process[68], the increase of the stability of macroradicals when the polymer is cross-linked[121,122], the identity in many instances of the activation energy for the destruction of macroradicals and the activation energy for the segmental movements in the polymer measured by NMR (see the references in the review of Pudov and Buchachenko[7]) §, the increase in the rate of destruction of macroradicals in three-dimensional polymers with increase of the length of the oligomer block[123], etc.

Two methodological procedures, whereby the mobility can be subjected to a controlled variation within wide limits, based on the change of the external pressure and the plasticisation of the polymer by chemically inert solvents, have been used recently in the study of the influence of molecular mobility on the kinetics of the destruction of macroradicals.

In amorphous polymers—polystyrene[24], poly(vinyl acetate),[124] poly(methyl methacrylate),[125] polyamides[126], and polycarbonate[127]—the constant k_t decreases with increasing pressure at temperatures in excess of T_g (in some cases by a factor of 10^2–10^3 at $p \cong 10^4$ atm). Below T_g, the influence of p on k_t is comparatively small. The nature of the dependence of k_t on p is such (Fig.3) that the greatest effect is observed at comparatively low pressures p; at each temperature above T_g there is a critical pressure p_{cr}, above which k_t depends only slightly on p. At $p < p_{cr}$ the dependence of k_t on p is described by the relation[129]

$$k_t = A_0 \exp[-(E + pV^*)/RT] \quad , \qquad (18)$$

where V^* is the activation volume and E sometimes changes as the pressure is altered[25,129].

Although the specific cause of the influence of p on k_t in each case is not known exactly, a common factor is apparently the fact that the pressure affects the kinetics of the destruction of macroradicals via molecular mobility. With increase of pressure, the density of the polymer also increases, which lowers the intensity of molecular movements, this being manifested particularly by an increase of T_g [for example, in poly(methyl methacrylate) $dT_g/dp = 2 \times 10^{-2}$ K atm^{-1} [129]], a decrease of the free volume, a decrease of the rotation frequency of a paramagnetic probe[133], etc. Eqn.(18) shows that an increase of p affects k_t in the same way as a decrease of temperature. Presumably the glass point is attained at $p = p_{cr}$.

The variation of the external pressure constitutes an extremely promising instrument for investigating the mechanisms of processes involving the destruction of macroradicals (and apparently also other radical reactions in solid polymers), particularly in a simultaneous study of molecular mobility. For example, in the basis of the data of Szocs and Plack[25], Szocz and Rostasova[129] concluded that there are two mechanisms of the destruction of terminal radicals in poly(methyl methacrylate). In the region of low pressures and high temperatures (high mobility) the destruction process is characterised by $E = 29$ kcal mol^{-1} and $V^* = 70$ Å^3 and the destruction apparently takes place as a result of physical diffusion; in the region of high pressures and low temperatures (low mobility) $E = 17$ kcal mol^{-1}, $V^* = 7.5$ Å^3, and the free valence most probably migrates with participation of the light radicals formed on dissociation of the macroradicals. The study of the influence of pressure on the kinetics of the destruction of the radicals can also yield information about the localisation of the radicals in amorphous-crystalline polymers. Since pressure alters the molecular mobility virtually only in the

§This agreement between the activation energies should, incidentally, be treated with much caution, because radicals are sometimes localised in the crystalline phase of the polymer, while data for the mobility refer to the amorphous phase.

amorphous phase, the weak dependence of k_t on p at temperatures above T_g indicates the localisation of the radicals in the crystallites[129].

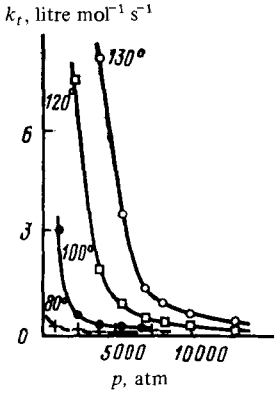


Figure 3. Dependence of k_t for terminal macroradicals in poly(methyl methacrylate) on pressure at different temperatures[125].

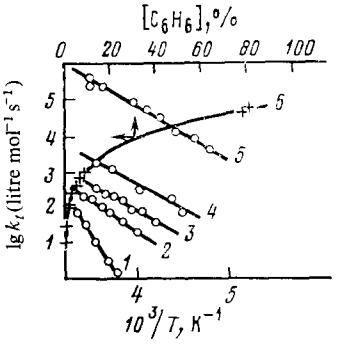


Figure 4. Temperature dependence of k_t for peroxy-radicals in polystyrene for different contents of benzene (%): *1*) 0; *2*) 2; *3*) 5; *4*) 12; *5*) 90; *6*) dependence of k_t on the benzene content at 270 K.[66]

The plasticisation of the polymers exerts a significant influence on the kinetics of the destruction of macroradicals. Thus the destruction of peroxy-radicals in polystyrene[66] (Fig. 4) and polypropylene[62,132] is greatly accelerated by the addition of comparatively small amounts of aromatic solvents, while the destruction of macroradicals in cellulose is accelerated by the addition of water[133]. The accelerating effect can be explained solely by an increase of molecular mobility. The variation of k_t in solid polypropylene in the presence of *o*-dichlorobenzene is correlated with the rotation frequency of the paramagnetic probe[132]. Table 5 shows that the increase of k_t is accompanied by a decrease of the activation energy and the pre-exponential factor; at fairly high concentrations of the additive these quantities approach the liquid-phase values.

The results of the consideration of the kinetics of the destruction of macroradicals are presented in Table 6. The operation of one of the mechanisms for the migration of the free valence in a specific system, discussed above, depends on the ratio of two factors: the intensity of the molecular movements in the polymer and the reactivity of the macroradicals. If the reactivity of the macroradicals is low and the intensity of the segmental movements is very great, the free valence will migrate mainly as a result of physical diffusion. This situation apparently obtains in elastomers above T_g and in highly plasticised polymers. In other cases physical diffusion leads to a very slow migration and cannot as a rule compete with "chemical" diffusion. When the free valence transfer reaction is fairly effective (high values of k_p), one may expect that the migration will take place via a relay-diffusional mechanism or, in the specific instance where the mobility is frozen to a large extent, via the trivial relay mechanism. If, finally, the macroradicals tend to dissociate or low-molecular-weight chain transferring agents are present in the system, the dominant mechanism of the migration will involve processes with participation of light radicals. Such migration mechanism ensures, in principle, the highest absolute rates of destruction of macroradicals.

Table 5. The influence of added aromatic solvents on the kinetics of the destruction of peroxy-macroradicals in solid polyolefins.

Low-molecular-weight additive	$(k_t)_0$, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k_t^*, litre mol^{-1} s^{-1}	Refs.
	Polypropylene			
—	$3.2\cdot10^{21}$	28.5	4	[62]
~2.5 M benzene	$5.6\cdot10^{13}$	14.5	$1.2\cdot10^3$	[62]
0.8 M *o*-dichlorobenzene	—	—	45	[132]
	Polystyrene			
—	10^{14}	17.6	12.5	[66]
0.6 M benzene	$3.2\cdot10^7$	6.3	$8\cdot10^2$	[66]

*The values of k_t at 25 °C are quoted.

Table 6. Characteristics of the valence migration processes in a solid polymer.

Migration mechanisms	Factors determining migration mechanism: segmental mobility (D, λ_r)	k_p	presence of low-molecular-weight chain transferring agents (k_1[rH])	tendency of macroradical to dissociate (k_s)	Parameter determining rate of migration	Factor influenced by molecular mobility
Physical diffusion	high	low	absent	low	D_2	D
Trivial relay	low	high	absent	low	$k_p\lambda_s^2$	k_p
Relay-diffusion mechanism	high	high	absent	low	$k_p\lambda_c^2$	k_p, $\bar{\lambda}_c$
With participation of light radicals:						
(a) chain transfer to low-molecular-weight admixture	comparatively low	low	present	low	k_1[rH] D_0	k_1, D_0
(b) dissociation of macroradicals	comparatively low	low	absent	high	$k_s D_0$	D_0

It is clear from the foregoing that the mechanism of the migration of the free valence is actually determined not only by the nature of the polymer and temperature but also by the type of macroradical, the localisation of the radicals in the amorphous or crystalline phases of the polymer, the presence of low-molecular-weight admixtures (plasticisers or chain transferring agents), etc.

The last column of Table 6 shows the parameters through which molecular mobility influences the kinetics of the destruction of macroradicals as a function of the migration mechanism. Furthermore, in each specific instance it is as a rule impossible to specify the "channel" for the exertion of the influence, because, as we have seen, it is fairly difficult to establish reliably the migration mechanism.

V. REACTIONS OF MACRORADICALS WITH MACROMOLECULES: $\dot{R}_1 + R_2H \rightarrow R_1H + \dot{R}_2$

Since both reactants are in a single "cage", the reactions of this type always proceed under kinetic conditions. At low temperatures (as a rule below T_g), where the destruction of radicals is still inappreciable, the reactions of macroradicals with macromolecules can be investigated directly, by following the concentrations of $\dot{R}_1$ and $\dot{R}_2$ by EPR. The reactions of terminal radicals in polyethylene[134]

$$\sim CH_2\dot{C}H_2 + \sim CH_2CH_2CH_2 \sim \rightarrow \sim CH_2CH_3 + \sim CH_2\dot{C}HCH_2 \sim$$

and the reactions of peroxy-radicals (chain propagation in oxidation)

$$R\dot{O}_2 + RH \rightarrow \dot{R} + ROOH \qquad (19)$$

in polyethylene, polypropylene[135], polyethylene–urea complexes[136], polystyrene[67,88], poly(methyl methacrylate)[10,67], polycaproamide, and polyacrylonitrile[67] have been investigated in this way. The $R\dot{O}_2 \rightarrow \dot{R}$ transition at low temperatures is as a rule described in terms of stepwise kinetics.

The quantity k_p for $R\dot{O}_2$ can also be obtained from the kinetics of the chain oxidation. The rate of oxidation w_{O_2} is given by the following expression on the assumption of fairly long chains:

$$w_{O_2} = \frac{k_p}{\sqrt{k_t}}[RH]\sqrt{w_0} \quad . \qquad (20)$$

If the rate of initiation w_0 is known, then it is possible to find the parameter $k_p/\sqrt{k_t}$ with the aid of Eqn.(20). Independent measurements of the termination rate constant k_t are necessary for the determination of k_p. The relevant data are presented in Table 7.

The most detailed information has been obtained for polypropylene. The quantities $k_p/\sqrt{k_t}$, measured at different temperatures and using different initiators, are fairly similar. The discrepancies between the k_p are very significant owing to the considerable discrepancies between the k_t in different studies.

In principle, k_p can be calculated from k_t for the destruction of macroradicals subject to the condition that the migration of the free valence is caused by "chemical" diffusion. However, even if the migration mechanism has been established reliably (which can be done, as already stated above, in comparatively rare instances), the calculation of k_p involves large errors, because the necessary parameters [for example, the elementary jump $\bar{\lambda}_s$ for the relay-diffusional mechanism of the migration of the free valence—see Eqn.(6)] are usually estimated very approximately.

Thus the information about the rate constants for reactions of macroradicals with macromolecules is so far fairly limited and refers virtually only to the reactions of peroxy-radicals.

We shall consider the influence of molecular mobility on the kinetics of reaction (19). Since both reactants are always in direct contact, one may consider here the influence of mobility solely on their interaction in the cage.

In the crystalline regions of isotactic polypropylene the radicals $R\dot{O}_2$ are destroyed ~10^4 times more slowly than in the amorphous regions and the transition $R\dot{O}_2 \rightarrow \dot{R}$ hardly occurs[53], although the rate constant for reaction (19) in the amorphous phase is extremely large[84]. Thus at 80 °C $k_p = 1.5 \times 10^{-1}$ litre mol^{-1} s^{-1}, which corresponds to an average reaction time $1/k_p[RH] \cong 0.3$ s. Apparently the only cause of the enormous difference between the reactivities of $R\dot{O}_2$ in the crystalline and amorphous phases is the difference between the intensities of the molecular movements.

It has been shown[143,144] that the rate of oxidation of polypropylene diminishes and the relative decrease of stability after oxidation in the presence of the same amount of absorbed oxygen is smaller when the system is oriented. This apparently implies that the chain propagation rate constant k_p for strained polymer chains with a limited mobility is significantly lower than for the unstrained chains.

The results of the study of reaction (19) in amorphous polystyrene in an inert atmosphere below T_g are even clearer[88]. At 210–293 K the process is described in terms of stepwise kinetics with a hyperbolic initial distribution of peroxy-radicals with respect to rate constants. Thus peroxy-radicals of identical chemical nature differ greatly in their reactivities. Analysis of the stepwise kinetics makes it possible to find the limits of the distribution of $(k_p)_{max}$ and $(k_p)_{min}$ and of the corresponding activation energies (Table 7). It is of interest that the quantity $(k_p)_{max}$ is fairly close to the rate constant for the reaction of a low-molecular-weight analogue of polystyrene (cumene) with its peroxy-radical in the liquid phase[33].

The physical significance of the stepwise kinetics in the given instance is that at a given temperature the more active radicals are "burnt off" more rapidly with k_p close to $(k_p)_{max}$; as a result, the distribution curve shifts towards radicals with $(k_p)_{min}$ (Fig.5) and the overall rate of the process is sharply retarded. An analogous phenomenon is observed in poly(methyl methacrylate).[10] Evidently any influences on the polymer promoting the restoration of the initial distribution will "restore" the initial rate of reaction. This has been achieved[88] by a brief dispersion of the specimen, in which the active radicals have been "burnt off", at 77 K¶.[12] The dispersion results in relative migrations of macroradicals and macromolecules and in a change of the local environment of the radical and of molecular mobility in the vicinity of the radical; in other words, the distribution functions with respect to k_p are mixed, which results in the restoration of favourable relative orientations of the radical and the surrounding macromolecules from the standpoint of reaction (19). When reaction (19) is carried out in an atmosphere of O_2, "chemical" mixing of the distribution function takes place[10,88] as a result of the generation of new peroxy-radicals in the

¶At 77 K reaction (19) does not proceed even under dispersion conditions owing to the presence of a large activation barrier.

Table 7. The values of $k_p/\sqrt{k_t}$ (litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$) and of the rate constants k_p (litre mol^{-1} s^{-1}) for the reaction $R\dot{O}_2$ + RH → $\dot{R}$ + ROOH in solid polymers (at 80 °C).

Polymer*	Oxidation conditions (initiator, t, °C)	$(k_p/\sqrt{k_t})$	E, kcal mol^{-1}	$(k_p/\sqrt{k_t})$	References	$(k_p)_0$	E, kcal mol^{-1}	k_p	References
PE	dicumenyl peroxide 110÷130	$5.6\cdot10^3$	21.2	$4\cdot10^{-5}$	[138]	$6.5\cdot10^{16}$	30.5	$7.7\cdot10^{-3}$	**
PE	in urea clathrate compounds, 70–108	—	—	—	—	—	24.6	—	[136]
a-PP	di-t-butyl peroxy-oxalate, 45–63	$3.1\cdot10^2$	8.5	$1.8\cdot10^{-3}$	[64]	$1.1\cdot10^9$	15.0	$5.5\cdot10^{-2}$	[64]
a-PP	benzoyl peroxide, 76–105	4.8	6.2	$6.9\cdot10^{-4}$	[139]	$1.6\cdot10^7$	12.1	0.54	[139]
i-PP	autoxidation,	$1.7\cdot10^2$	9.0	$4.5\cdot10^{-4}$	[140]	$3.4\cdot10^6$	9.0	0.89	[140]
i-PP	110–140 autoxidation, 120–140***	$6.2\cdot10^4$	12.8	$7.5\cdot10^{-4}$	[141]	—	—	—	—
i-PP	photo-oxidation, 20–140***	$1.4\cdot10^2$	8.5	$4\cdot10^{-4}$	[142]	—	—	—	—
i-PP	PP hydroperoxide, azobisisobutyro-nitrile, 44–92****	17	6.6	$8.1\cdot10^{-4}$	[84]	$9.6\cdot10^{11}$	21.0	0.1	[82]
PB-1	benzoyl peroxide, 76–119	$9.1\cdot10^5$	18.0	$6.5\cdot10^{-4}$	[139]	$1.3\cdot10^{11}$	18.0	0.89	[139]
P-4-MP-1	benzoyl peroxide, 85–95	10^7	20	$4\cdot10^{-4}$	[139]	—	—	—	—
PEO	radiation oxidation, 25	—	—	$3.3\cdot10^{-4}$(25′)	[137]	—	—	—	—
PS(max)	−63÷+20					$3.7\cdot10^7$	10.3	0.7(20°)	[88]
PS(min)****	—					$1.4\cdot10^{12}$	21.0	$3\cdot10^{-4}$(20°)	[88]
PMMA(max)*****	0÷−20					$8\cdot10^6$	12.0	$8\cdot10^{-3}$(20°)	[10]
PMMA(min)*****						$1.4\cdot10^{14}$	25.8	$8\cdot10^{-6}$(20°)	[10]

*PB-1 = polybut-1-ene, P-4-MP-1 = poly-4-methylpent-1-ene, and PEO = poly(ethylene oxide); for the significance of the remaining abbreviations for the polymers, see Table 3.

**The constant $k_t = 1.4 \times 10^{16} \exp(-18500/RT)$ (litre mol^{-1} s^{-1}) taken from Davis et al.[61] was used.

***Recalculated for the amorphous phase on the assumption that the degree of crystallinity is 0.6.

****The constant $k_t = 3.2 \times 10^{21} \exp(-28500/RT)$ (litre mol^{-1} s^{-1}) taken from Roginskii and Miller[62] was used.

*****On the basis of the "stepwise" kinetics of the transition $R\dot{O}_2$ → $\dot{R}$ in an inert atmosphere.

reaction

$$\dot{R} + O_2 \rightarrow R\dot{O}_2 \quad .$$

"Thermal" mixing of the distribution functions is also possible.

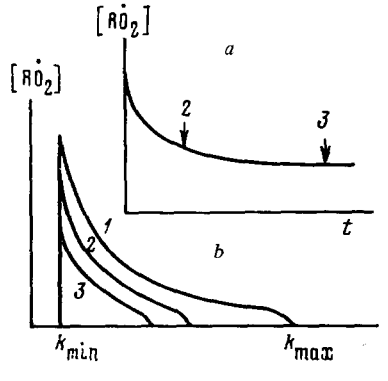


Figure 5. *a*) Kinetics of the reaction $R\dot{O}_2$ → $\dot{R}$ in polystyrene; *b*) changes in the curve illustrating the range of rate constants for $R\dot{O}_2$ reactions in the course of the kinetic experiment (according to Radtsig's data[10]).

Molecular mobility influences the rate of reaction (19) also in "softer" polymer matrices where the stepwise kinetics are not as yet observed. Thus k_p increases significantly in the oxidation of solid polypropylene at 25 °C in the presence of the chemically inert *o*-dichlorobenzene, the growth of k_p being correlated with the increase of the rotation frequency of the paramagnetic probe characterising molecular mobility[132].

VI. PHYSICAL MECHANISMS OF THE INFLUENCE OF MOLECULAR MOBILITY ON REACTIVITY

As shown in the previous sections, one of the characteristic features of radical reactions in solid polymers is that their rate is frequently related to the kinetics of molecular movements even under kinetic conditions. This is manifested both in reactions of macroradicals and macromolecules and in processes involving low-molecular-weight substances. If the treatment is confined to processes whose rates are not limited by the encounters of the reactants, it is possible in principle to set up two physical models relating the kinetics of chemical reactions in polymers to molecular mobility.

In the first model, which can be called the *delayed rehybridisation model*[146], it is assumed that the macrorelaxation time in polymers is long compared with the duration of the chemical step. For example, in the abstraction of a hydrogen atom from an sp^3-carbon atom in the polymer chain the hybridisation should change to sp^2, this being accompanied by a change in valence angles (from 109° to

120°) and bond lengths; the latter requires structural relaxation. In the liquid and gas phases both steps—the abstraction of a hydrogen atom and rehybridisation—take place sychronously, while in a polymer matrix they are separated in time. As a result of the low rate of structural relaxation in polymers, the energetically most favourable activated complex cannot be formed during the reaction step. The process therefore follows a higher profile of the potential energy surface compared with the liquid (gas) phase, which leads in its turn to an increase of the activation energy and a decrease of the reaction rate constants. With increase of mobility, structural relaxation is facilitated and the delay of rehybridisation is correspondingly diminished; as a result, the activation energy falls and the rate constant increases, approaching the liquid-phase values.

There is no direct evidence for the reality of the delayed rehybridisation model, which remains hypothetical. Although many kinetic features of radical reactions in solid polymers can be accounted for in the framework of this model, some of its consequences are not fulfilled. In particular the model predicts a significant decrease in the rate constants for radical substitution reactions only in processes involving the atoms in the main chain of the macromolecule, whereas it has been observed, as shown above, that the rate constants for reactions involving the side groups of macromolecules as well as low-molecular-weight substances are lower than in the liquid phase.

We shall now consider the second model. For the chemical reaction to occur, a rigorously defined orientation of the reacting species and their elements (for example, the unpaired electron orbital and the chemical bond) is necessary. Thus the abstraction of a hydrogen atom by a free radical requires that the bond undergoing association should be arranged coaxially with the unpaired electron at a distance of 1.5–2.0 Å. In other words, it is necessary that the state preceding the reaction (the prestart state) should be located on the reaction coordinate. To attain this state, a reorientation of the reacting species, as a result of translational and rotational diffusion, is necessary. This model (we shall call it the *structural-orientational correspondence model*) can in principle explain also the marked dependence of the reaction rate on the molecular dynamics of the polymer and its microstructure.

Many characteristic features of the kinetics of radical reactions in solid polymers can be naturally explained within the framework of this model: the sensitivity of the kinetics to the structure and morphology of the polymers, the decrease of the rate constants and the increase of the activation energies compared with the liquid phase, and the relation between the kinetics and molecular mobility. Solid polymers are structurally inhomogeneous systems with a broad distribution with respect to the frequencies and amplitudes of molecular movements. Such frequency-amplitude "polychromaticity" leads to a kinetic "polychromaticity"—a wide range of rate constants and activation energies for the reactants.

With increase of temperature, the molecular movements are gradually "unfrozen"; as the temperature increases, movements on a larger scale are "unfrozen". As a result of this, the effective activation energy (or the range of activation energies) depends on the temperature. A kinetic consequence of this change is the compensation effect and the anomalously high activation energies and pre-exponential factors, which lack physical significance. This also applies to the rotational[131] and translational[147] diffusion of low-molecular-weight substances, which are likewise controlled by the molecular dynamics of the polymer. It is striking that, if the Arrhenius parameters of the chemical reaction[65] or the rotational diffusion of the paramagnetic probe[131] in solid polymers have been obtained under the conditions of a constant intensity of the molecular movements of the polymer, then the activation energies and pre-exponential factors approach the "normal" liquid-phase values.

However, when specific versions of the structural-orientational correspondence model are considered, considerable difficulties are encountered.

(1) In the model of "black spot" spheres[56,148–151] it is assumed that the reacting species exhibit a marked anisotropy in their reactivity. In other words the reaction centre occupies only a small proportion (the "black spot") of the surface of the species. In order that contact between the species in the cage should be accompanied by reaction, their mutual orientation involving the coincidence of the "black spots" is necessary. Analysis of the results of studies[148,150] in which the above model has been considered most rigorously shows that the dependence of the effective rate constant for a bimolecular reaction on the rotation frequency of the reactants can be observed in those cases where the rate of reaction is limited by the encounters of the reactants, i.e. occurs under diffusional conditions. However, as already stated, such dependence is observed experimentally also for reactions which clearly take place under kinetic conditions.

A similar dependence is to be expected also when the required orientation (contact between the "black spots") cannot be realised, in principle, during the existence of the pair†. This situation is in its turn possible if the rotation frequency of the reacting species in the pair is significantly lower than the frequency of their translational migrations (the latter determines the frequency of the decomposition of the pair) or if the fraction of the required orientations is low (this is equivalent to a low pre-exponential factor).

Comparison of the rotation frequencies of stable nitroxy-radicals with the frequencies of their translational jumps in solid polymers[152] shows that the first case apparently does not occur. The second case can occur, according to the data of Griva et al.[56] for the reaction involving the addition of a nitroxy-radical to methylenequinone in the matrices of solid polyolefins: the pre-exponential factor in the expression for the rate constant for this reaction in the liquid phase is only ~10^2 litre mol^{-1} s^{-1}; however, it must be admitted that the reactions with such low pre-exponential factors are nevertheless encountered fairly rarely.

Thus the versions of the "black spot" model considered cannot as a rule explain the experimental relation between the rate constants for bimolecular reactions in solid polymers and the molecular mobility.

(2) The *stepwise orientation model* can be represented by the following scheme:

$$A + B \underset{\nu_t}{\rightarrow} [A \ldots B]_1 \underset{\nu_r}{\rightarrow} [A \ldots B]_2 \underset{\nu_r}{\rightarrow} [A \ldots B]_n \xrightarrow{k} \text{products}.$$
$$\uparrow \qquad\qquad |\nu_t \qquad\qquad |\nu_t \qquad\qquad |\nu_t$$

The pair $[A \ldots B]_1$ formed can either dissociate as a result of the translational jump of one of the reactants at a frequency ν_t or can be converted into another pair $[A \ldots B]_2$ with a different orientation of the reactants, etc. The rotational movement of the partners in the pair at a frequency ν_r "sorts through" the orientational states of the pair until the latter is in the "starting" state $[A \ldots B]_n$ with the orientation of the reactants favourable for reaction. The

†Otherwise the pair of reacting species is able to pass through all the possible orientational states and the rate of chemical reaction no longer depends on the rotation frequencies.

effective rate constant for a bimolecular reaction is

$$k_{\text{eff}} = \frac{k\nu_t}{k+\nu_t}\left(\frac{\nu_r}{\nu_r+\nu_t}\right)^n ,$$

where n is the average number of orientational states preceding the "starting" state $[A...B]_n$. The dependence of k_{eff} on the intensity of molecular movements involves mainly the numerator $[\nu_r/(\nu_r + \nu_t)]^n$.

(3) The "*rigid cage*" model[151,153] postulates that the orientation of the partners in the cage favourable for reaction has a statistically low probability, since it requires that a potential barrier be overcome. In fact one assumes here that the species in the cage are in thermodynamically favourable orientations, but the reaction takes place in other thermodynamically unfavourable states. It is postulated that, when molecular movements are "unfrozen", the statistical weight of the favourable orientations increases. This model is in essence similar to the previous one, the difference consisting in the fact that it involves a statistical thermodynamic and not a kinetic treatment.

The "rigid cage" and "stepwise orientation" models, as well as the "black spot" model discussed above, can operate under conditions where the rate-limiting stage of the process is the attainment of a favourable relative orientation of the reacting species in the cage as a result of their rotational diffusion. As already stated, this is apparently improbable.

The situation might be saved by the fact that the rotation of the species in the polymer matrix is in general anisotropic, i.e. the rotation frequencies relative to different molecular axes are different. One might assume that the rotation about an axis which requires the overcoming of a comparatively large potential barrier and is therefore slow is important for the attainment of a favourable orientation of the reactants in the cage and not rotation in general (which, as already stated, takes place at a higher frequency in solid polymers than translation). In other words, it is necessary to assume that the activation energies for rotation about different axes are different, i.e. that the anisotropy of the rotation depends on temperature.

An experimental test[154] did not confirm the latter hypothesis. It was found that the rotation of the nitroxy-radicals in polymer matrices is indeed anisotropic (incidentally the rotation frequencies about different axes differ by not more than an order of magnitude even for non-spherical radicals), but the anisotropy is independent of temperature and hence the activation energies for rotation about different axes are the same. Thus even allowance for the anisotropy of the rotation in the structural-orientational correspondence model does not eliminate its difficulties.

(4) Finally mention must be made of the *free volume model*[155]. It postulates that the reaction takes place only in certain local microregions of the polymer in which the free volume fluctuates and for this reason the local molecular movements are "unfrozen". This model is partly phenomenological; it does not deal in detail with the kinetics of the elementary reaction step, but relates the effective rate constants to physical parameters of the polymer such as compressibility, coefficient of thermal expansion, etc. An impression is created that the free volume model can explain the dependence of the rate of reaction on mobility only under the conditions of a low intensity of the molecular movements at temperatures below T_g, while the greatest difficulty arises in explaining this dependence in "soft" polymer matrices at temperatures significantly above T_g.

Thus the problem of the physical causes of the relation between the chemical kinetics and the molecular dynamics in solid polymers for reactions under kinetic conditions in essence remains open.

* * *

The problems considered in the review, namely the relation between the kinetics of radical reactions and the molecular dynamics of the polymer, the kinetics and mechanisms of the migration of the free valence, and the physical models of radical reactions, are fundamental key problems, on the solution of which further development of the given field of chemical kinetics, i.e. the kinetics of radical reactions in solid polymers, largely depends.

In assessing the general state of this field, one must recognise that, despite extremely extensive experimental data, the majority of the problems can be discussed at the present time mainly at the phenomenological level. The most important tasks are a detailed investigation of molecular dynamics in polymers and its relations with chemical kinetics, the elucidation of the true mechanism of radical processes, and an increase of the accuracy and reliability of kinetic information. All these require much effort and in particular the development of new research techniques and new experimental approaches.

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Quantitative Analysis of Influence of Structure on Reactivity of Four-coordinated Phosphorus Compounds

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A survey of the systematic application of correlation analysis to structural effects in organic compounds of four-coordinated quinquevalent phosphorus showed that the axiomatics of modern analysis (including possible types of intramolecular interaction between fragments of organic molecules and mathematical models of such interaction) will provide an adequate description of the effects of substituents attached to the phosphorus atom. Quantitative resolution into individual components of the structural effects governing the strengths of organophosphorus acids indicates that the widely used σ^{ph} constants are complicated in nature, comprising contributions by inductive, steric, and resonance interactions of substituents with the phosphorus atom. A list of 104 references is included.

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I. INTRODUCTION

The intensive development of the chemistry of organophosphorus compounds is due to their widespread use in industry, medicine, agriculture, and other fields. Identification of the properties of practical importance and especially problems involved in the planned synthesis of such compounds make necessary further broadening and deepening of theoretical research in organophosphorus chemistry. One fundamental problem common to the whole of organic chemistry—the search for quantitative relations describing the effects of various factors on the reactivity and the physical and physicochemical properties of compounds—has now been satisfactorily solved in terms of correlation analysis[1-3]. Correlation equations are widely employed also in the chemistry of organophosphorus compounds. As early as 1953 Jaffe et al. showed that the Hammett equation will give a good description of the pK_a of aromatic phosphonic acids[4]. Later Kabanchik[5] found that this equation is applicable to the most diverse organic acids of phosphorus, provided that special constants σ^{ph} are used for *P*-substituents. These constants and their resolution into inductive and resonance components[6] have provided satisfactory descriptions of many types of reactions occurring both at the phosphorus atom and in a side-chain, and also of various physical and physicochemical properties of organophosphorus compounds[7,8]. Since, like the Hammett σ-constants, these are empirical constants, simple equations containing a single parameter can be employed, which has proved convenient for solving many problems of organophosphorus chemistry. However, their use automatically excludes the possibility of comparing, on the basis of correlation analysis and the corresponding equations, reaction series of organophosphorus compounds with those involving other organic or hetero-organic compounds.

Qualitative ideas on possible universal types of interaction (and their mechanisms) between fragments of organic molecules were formulated in theoretical organic chemistry long ago[9]. Correlation analysis, having established a list of possible interactions, conferred a quantitative form on these ideas[1,10] (mathematical models of individual types of interaction), by regarding any interaction as a departure from additivity[11-13] and introducing measures of the ability of substituents (molecular fragments) to undergo various types of interaction. Inspection of a large quantity of factual information on the effect of substituent structure on reactivity of organic compounds led to the formulation of axioms of correlation analysis, which reduced essentially to the following postulates.

1. Three types of intramolecular interactions—inductive, steric, and resonance—are possible between uncharged fragments (substituents) in organic molecules.
2. The change in free energy accompanying reaction or activation can be represented quite accurately as the sum of contributions by these interactions (Taft's first postulate[10]).
3. The principle of linearity of free energies applies to each of these contributions (Taft's second postulate[10]).
4. The contribution by any interaction between two structural fragments is proportional to the product of the corresponding constants characterising the ability of the fragments to undergo the given type of interaction (the Hine–Pal'm postulate[11-15]).
5. In addition to the above types of interaction, charged fragments can also have electrostatic interaction, described by an appropriate mathematical model[1,16] and inversely proportional to the macroscopic dielectric constant of the medium (Palm's postulate).

The scales of the ability of various substituents to undergo the above types of interaction (measured by the constants σ^*, E_S, σ^0, σ^+, etc.) have been calculated from experimental data for different series with variation in substituents mainly at a carbon atom. However, it has now been firmly established that these axioms and also the corresponding measures of the capacity of substituents for various types of interaction can be satisfactorily applied to the quantitative description of diverse kinetic and equilibrium series in which substituents are varied at atoms other than carbon—sulphur, nitrogen, oxygen, silicon, etc.—as is indicated by ample

practice of correlation analysis[1-3,17,18]. Special investigations[1,19-26] have been made on problems associated with the limits of applicability of these axioms (completeness of the list of interactions, universality of the corresponding measures (constants), etc.).

Systematic application, to the enthalpies of formation of diverse organic compounds in the gas phase, of the principle of polylinearity[11,27] together with the above postulates not only has enabled a fundamentally new and accurate scheme of calculation to be constructed for these most important standard thermodynamic characteristics of compounds but also has shown that the mathematical models of correlation analysis for individual types of interaction agree well with the corresponding contributions to heats of formation[19-23].

Nor have accurate measurements of the acidity and basicity of various classes of organic compounds in the gas phase necessitated a fundamental revision of the main concepts of correlation analysis (if the problem of the nature of the influence of alkyl groups is disregarded), since a good correlation usually exists between structural effects on dissociation in the gas phase and in solution[28-34], indicating that structural effects on the strengths of acids and bases in the gas phase and on the capacity of their neutral and ionic forms for solvation are of the same type. It would have been difficult to expect a different result in these terms, since correlation equations provide an adequate description of the influence of structural factors on the strengths of organic acids and bases in the most diverse pure media and their mixtures which vary markedly in dielectric properties, polarisability, and capacity for various types of specific solvation[18,25,26,35]. The nature of the influence of alkyl groups, however, has long been a matter of controversy in the correlation analysis of structural effects in the liquid phase[1,2,15,19,20,36-39], as also the physical nature of the inductive (polar) effect. But there is no doubt about the actual existence of such effects.

The satisfactory correlation of the properties of organophosphorus compounds with the σ^{pH} constants indicates that the principle of the linearity of free energies can be widely applied to describe the influence of *P*-substituents on the reactivity of these compounds. Isolated studies have shown also that certain of their properties can be described in terms of correlation relations based on the "carbon" constants of the substituents[4,40-44]. However, the fundamental applicability of the entire axiomatics of correlation analysis to the structural effects of *P*-substituents has remained an open question until recently, as also the limits of applicability of the axiomatics in organophosphorus chemistry. Other nontrivial questions that have not been settled are whether (i) the list of possible types of interaction and (ii) the mathematical models for individual types are adequate to describe the effects of such substituents.

Attempts by Pal'm[45] and by Charton[46] to solve these problems did not give unambiguous results[8]. The aim of the present Review consists in setting out the main results of investigations[47-55] which the Reviewers regard as providing answers to the above questions and leading to some unexpected but logically self-evident conclusions. In view of the great diversity of the valency and coordination states of the phosphorus atom in various organophosphorus compounds, only the effects of substituents attached to a four-coordinated quinquevalent phosphorus atom of the type $\gtrdot$PO have been considered, since such compounds have been most widely investigated in terms of their reactivity and various physicochemical properties, and the correlation of these properties with structure has also been studied. Furthermore, analogies for processes occurring at such a group can be found in classical organic chemistry, in particular among those taking place at a carbonyl group[56-62].

Because of the wide applicability of σ^{ph} constants in organophosphorus chemistry an analysis has been made of them[47-55] and also of the dissociation of various acids of general formula XYPOOH, the standard reaction series for their determination. Furthermore, a systematic comparison has been made of the influence of substituents on reaction centres containing carbonyl and phosphoryl to reveal specific structural effects characteristic of the phosphorus atom alone; the combined influence of substituents attached to a four-coordinated phosphorus atom has been examined.

II. EQUATION FOR pK_a OF ACIDS XYPOOH

On the above postulates the difference $\Delta\Delta G^0$ between the changes in free energy $\Delta G^0(XY)$ and $\Delta G^0(X_0Y_0)$ accompanying dissociation of the acids XYPOOH and X_0Y_0POOH can be written as the sum

$$\Delta\Delta G^0 = \Delta G^0(XY) - \Delta G^0(X_0Y_0) = \Delta\Delta G^0_{ind} + \Delta\Delta G^0_{ster} + \Delta\Delta G^0_{res}, \quad (1)$$

of contributions $\Delta\Delta G^0_{ind}$, $\Delta\Delta G^0_{ster}$, and $\Delta\Delta G^0_{res}$ by inductive, steric, and resonance interactions of the substituents X (X_0) and Y (Y_0) with the reaction centre and between themselves X and Y or X_0 and Y_0. The quantity $\Delta\Delta G^0$ corresponds to the change in free energy in the equilibrium proton transfer

$$XYP(O)OH + X_0Y_0P(O)O^- \rightleftharpoons XYP(O)O^- + X_0Y_0P(O)OH.$$

The quantities

$$\Delta\Delta G^0_{ind} = \Delta G^0_{ind}(XY) - \Delta G^0_{ind}(X_0Y_0), \quad \Delta\Delta G^0_{ster} = \Delta G^0_{ster}(XY) - \Delta G^0_{ster}(X_0Y_0), \quad \Delta\Delta G^0_{res} = \Delta G^0_{res}(XY) - \Delta G^0_{res}(X_0Y_0)$$

are the differences between the contributions by the corresponding interactions to the changes in free energy accompanying detachment of a proton from the acids XYPOOH and X_0Y_0POOH. In conformity with the practice of correlation analysis we adopt as standard substituent the methyl group: i.e. $X_0 = Y_0 = CH_3$.

In terms of the principle of polylinearity[1,27] and the homogeneity of inductive interaction[1]

$$\Delta\Delta G^0_{ind} = \Delta G^0_{ind}(XY) - \Delta G^0_{ind}(X_0Y_0) = -\alpha^*\Delta\sigma^*_{rc}\sum\sigma^* - \alpha^*\Delta Z^*\sigma^*_X\sigma^*_Y \quad (2)$$

where α^* is the universal constant[25] of inductive interaction,

$$\Delta\sigma^*_{rc} = \sigma^*(CH_3POOH) - \sigma^*(CH_3POO^-)$$

is the difference between the inductive constants of the reaction centre in initial and final states, and

$$\Delta Z^* = Z^*(\gtrdot POOH) - Z^*(\gtrdot POO^-)$$

is the difference between the conductivities of inductive interaction between X and Y through the reaction centre in its initial and final states. The first term in Eqn.(2) is the contribution to $\Delta\Delta G^0$ by inductive interaction of X and Y with the reaction centre†, and the second term by inductive interaction between X and Y through the reaction centre.

If the acid and its anion have a tetrahedral structure[63,64], it is obvious from symmetry considerations that the contribution

$$\Delta\Delta G^0_{ster} = \Delta G^0_{ster}(XY) - \Delta G^0_{ster}(X_0Y_0) = -\Delta a\sum E_s \quad (3)$$

† Here and subsequently. $\sum\sigma^*\left(\sum E_s\right) = \sigma^*_X + \sigma^*_Y\left(E_{sX} + E_{sY}\right)$.

where

$$\Delta a = a(CH_3POOH) - a(CH_3POO^-)$$

is the difference in sensitivity of the reaction centre, in initial and final states, to steric interaction with substituents#. Equation (3) contains no cross terms: i.e. contributions by steric interactions between substituents X and Y in the acid and in its anion are assumed to be similar (or equal) in magnitude, a hypothesis which has been confirmed[47].

Substitution of Eqns.(2) and (3) in (1) followed by conversion to pK_a values yields

$$pK_a(XYP(O)OH) = pK_a(Me_2P(O)OH) - \rho^* \sum \sigma^* - \gamma\sigma_X^*\sigma_Y^* - \delta \sum E_s + \Delta\Delta G^0_{res}/2.303RT \quad (4)$$

where

$$\rho^* = \alpha^* \Delta\sigma^-_{ph}/2.303RT;\ \gamma = \alpha^* \Delta Z^*/-2.303RT;\ \delta = \Delta a/2.303RT.$$

Hence, provided that all the above postulates are valid, the pK_a values of XYPOOH acids, in which X and Y are uncharged substituents, should be given by Eqn.(4).[47] With regard to experimental verification of this equation, the question of resonance interaction merits the special comment that, since hyperconjugation plays no great part[1,19] in the ground state of organic compounds, it was accepted[47-55] that aryl groups, αβ-unsaturated substituents, and substituents whose first atom is a heteroatom having a lone pair of electrons are capable of conjugating with an electron-deficient reaction centre of $-C$ type: all other substituents—alkyl groups, $X^1X^2X^3M[CH_2]_m$, $X^1X^2CH[CH_2]_m$, and $XCH_2[CH_2]_m$ (the X are various electronegative groups, and $m = 0, 1, 2, \ldots$)—were regarded as incapable of conjugation[19,47].

III. ANALYSIS OF σ^{ph} CONSTANTS

The dissociation of XYPOOH acids was chosen[5] as standard series for deducing σ^{ph} constants, and the hydrogen atom was adopted as standard substituent:

$$pK_a(XYP(O)OH) = pK_a(H_2P(O)OH) - \sum \sigma^{ph} \quad (5)$$

It follows from Eqns.(4) and (5) that the σ^{ph} constants of substituents incapable of conjugation with the reaction centre should be given by[47]

$$\sigma^{ph} = \sigma^{ph}(Me) + \rho^*\sigma^* + 0.5\gamma(\sigma^*)^2 + \delta E_s \quad (6)$$

The regression dependence

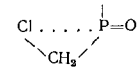
$$\sigma^* = -(0.938 \pm 0.036) + (1.151 \pm 0.076)\sigma^* - (0.199 \pm 0.031)(\sigma^*)^2 + (0.149 \pm 0.030)E_s$$

$$n = 25;\ R = 0.987;\ S_0 = 0.11 \quad (7)$$

has been found[47] for 25 such substituents. Here and subsequently n is the number of experimental points described by a given equation, $r(R)$ the (multiple) correlation coefficient, and $s_0(S_0)$ the (multiple) regression standard. All coefficients in the relation (7) are statistically significant, and from (6) the independent term is identical with $\sigma^*(CH_3)$.[7]

The reproducibility of pK_a values determined by potentiometric titration has been estimated[66,67] as 0.04–0.05 logarithmic unit. The pK_a values used[7] in calculating σ^{pH} have been measured at 20–25 °C, in which temperature range the divergence in estimates of pK_a for organic acids of phosphorus may reach estimates of pK_a for organic acids of phosphorus may reach ±0.03 lg unit[68]. In virtue of the law of the accumulation of errors the uncertainty in the calculation of σ^{ph} is thus at least ±0.09 lg unit. Furthermore, the σ^{ph} constants recommended[7] for use had been averaged over many reaction series, and such averaging replaces[17] the apparent reliability by considerable uncertainty in the constants. Consequently the regression (7) is close to adequacy.

In the resolution of σ^{ph} constants into inductive and resonance components σ^{ph}_{ind} and σ^{ph}_{res} non-zero resonance constants were ascribed[6,7] to many substituents and were not αβ-unsaturated and had no n-electrons on the α-atom. The especially high σ^{ph}_{res} values for mono-, di-, and tri-halogenomethyl groups were attributed[7,69] to a contribution by a transannular dative bond of type



However, such a bond was not detected[70] in the chlorine-35, bromine-79, and iodine-127 nuclear quadrupole resonance spectra of the compounds $(ClCH_2)_3PO$, $(ClCH_2)_2CH_3PO$, $(ICH_2)_3PO$, $(ICH_2)_2CH_3PO$, and $(BrCH_2)_2CH_3PO$. In terms of the regression (7) the resonance constants σ^{ph}_{res} for such substituents should be a combination of inductive and steric components (owing to incorrect resolution[6,7] of the σ^{ph} constants). In fact, for substituents described by regression (7) the relation

$$\sigma^{ph}_R = (0.059 \pm 0.046) - (1.202 \pm 0.042)\sigma^* + (0.237 \pm 0.050)E_s$$

$$n = 24;\ R = 0.9902;\ S_0 = 0.138$$

was found[47], from which only the point for cyanoethyl departs significantly.

Table 1. Values of $\overline{\Delta\sigma^{ph}}$ averaged over individual structural types of substituents*[48].

Type of substituent	m	$\overline{\Delta\sigma^{ph}}$
R_2N(R — Alk)	2	—0.79±0.06
PhO	1	—0.65
RO(R—H, Alk)	10	—0.62±0.02
RS(R — Alk)	4	—0.18±0.03
XC_6H_4(X—H, Alk, electroneg. subst.)	24	—0.07±0.01

*Here m is the number of substituents of the given structural type for which $\Delta\sigma^{ph}$ have been calculated.

Values of σ^{ph}_{calc} calculated by means of Eqn.(7) for substituents capable of conjugation are usually more positive than the experimental values σ^{ph}_{exp}: i.e. such substituents are characterised not only by inductive and steric effects but also by an additional effect that lowers the acidity of the compounds. This may be solely due to conjugation of the substituents with the reaction centre. On this basis the differences $\Delta\sigma^{ph} = \sigma^{ph}_{exp} - \sigma^{ph}_{calc}$ for these substituents were adopted as measures of their resonance capacity. For substituents of the same structural type calculated differences

Steric interaction is inhomogeneous[1,13,65], and therefore cannot be described by a mathematical model similar to that used for inductive interaction.

$\Delta\sigma^{ph}$ do not exceed the experimental uncertainty in the constants σ^{ph}_{exp}:[48] i.e. the ability of, for example, substituents RO, RS, and R_2N to conjugate is to a first approximation independent of R. Therefore average values $\overline{\Delta\sigma^{ph}}$ (Table 1) were taken[48] as the estimated capacities of such substituents for conjugation. An obvious correlation exists (Fig.1) between the $\Delta\sigma^{ph}$ values and the σ^{+}_{res} constants[24] representing the ability of the substituents to conjugate with a $-C$ type of reaction centre.

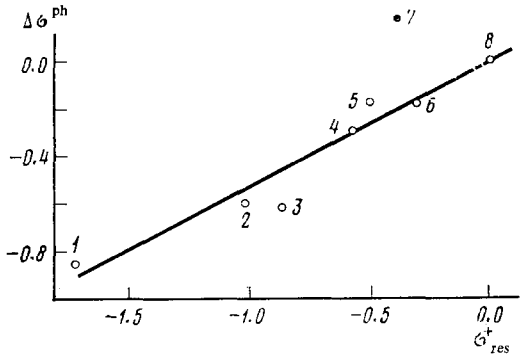


Figure 1. Correlation[48] between deviations $\Delta\sigma^{ph} = \sigma^{ph}_{exp} - \sigma^{ph}_{calc}$ and resonance constants σ^{+}_{res} for the substituents: 1) $(CH_3)_2N$; 2) CH_3O; 3) C_6H_5O; 4) F; 5) CH_3S; 6) C_6H_5; 7) Cl; 8) H.

The whole set of σ^{ph} constants (see compilation in Ref.48) is adequately described by the equation[48]

$$\sigma^{ph} = -(0.956 \pm 0.015) + (1.129 \pm 0.030)\,\sigma^{*} - (0.187 \pm 0.011)\,(\sigma^{*})^2 + (0.166 \pm 0.014)\,E_s - (0.952 \pm 0.44)\,\overline{\Delta\sigma^{ph}}$$
$$n=71;\ R=0.992;\ S_0=0.073\ . \qquad (8)$$

The estimated coefficients obtained in this regression, of the sensitivity of substituents to inductive and steric effects, coincide within the limits of their errors with the corresponding quantities in regression (7). The independent term, as Eqn.(6) requires, is identical with the $\sigma^{ph}(CH_3)$ constant. The coefficient accompanying the resonance contribution should be unity if $\overline{\Delta\sigma^{ph}}$ values have been introduced: the estimate of this coefficient in regression (8) is indeed close to unity.

Thus the above results[47,48] indicate that the σ^{ph} constants for *P*-substituents comprise inductive, steric, and resonance contributions that are adequately described in terms of the usual "carbon" constants σ^{*} and E_S and by means of $\Delta\sigma^{ph}$ values linearly related to the σ^{+}_{res} constants.

IV. INFLUENCE OF STRUCTURAL FACTORS ON STRENGTHS OF ACIDS XYPOOH

It has been shown above that the pK_a values of XYPOOH acids should be described by Eqn.(4), which itself should be defined by the pK_a of phosphinic acids, the pK_{a_1} and pK_{a_2} of phosphonic acids, and also all three pK_a of phosphoric acid if the fragment O^- is regarded as a substituent. In order to take into account the electrostatic interaction between two O^- substituents the electrostatic correction $\Delta pK_{el} = 1.2$ was calculated[49] from the equation suggested in Ref.16 and the geometry of the anion of phosphoric acid[63]. This correction was assumed to be constant for all phosphonic acids. The fundamental possibility of describing pK_{a_1}, pK_{a_2}, and pK_{a_3} by means of a single equation can be illustrated by the simple relation

$$pK_{a_3}(H_3PO_4) = 2pK_{a_2}(MeP(O)(OH)_2) - pK_a(Me_2P(O)OH) + \lg 3 - \lg 2$$

which follows from (4) and takes into account statistical corrections. This gives for $pK_{a_3}(H_3PO_4)$ an estimated 12.3, while the experimental value is 12.0–12.3.[71]

Table 2. Analysis of pK_a values (in water at 20–25 °C) by means of Eqn.(9).[49]

Coeff. or statistical criterion	Regression		
	№ 1*	№ 2**	№ 3***
a_0	3.075±0.055	3.075±0.54	3.122±0.046
a_1	−1.374±0.046	−1.275±0.046	−1.358±0.040
a_2	0.161±0.042	0.163±0.042	0.166±0.037
a_3	−0.230±0.027	−0.230±0.076	−0.230±0.024
a_4	1.259±0.077	1.250±0.076	1.221±0.084
a_5	0.271±0.076	0.263±0.091	0.256±0.041
a_6	3.242±0.054	4.486±0.041	3.160±0.041
a_7	1.815±0.079	1.813±0.079	1.790±0.078
n	72	72	109
R	0.9963	0.9976	0.9967
S_0	0.182	0.181	0.166

*Calculated disregarding compounds in which X and (or) Y = Ar.
**Calculated disregarding both compounds in which X and (or) Y = Ar and also the electrostatic correction.
***Calculated for the complete set of pK_a values (see compilation in Ref.49).

Table 2 lists results of an analysis[49] of pK_a values of XYPOOH acids given with statistical and electrostatic corrections by the equation

$$pK_a(XYP(O)OH) = a_0 + a_1\sum\sigma^{*} + a_2\sigma^{\bullet}_X\sigma^{\bullet}_Y + a_3\sum E_s + a_4 n_{RO} + a_5 n_{Ar} + a_6 n_{O^-} + a_7 n_{ArO} \qquad (9)$$

in which a_0–a_7 are the unknown coefficients (a_0–a_3 should include analogous coefficients in Eqn.(4) and a_4–a_7 are resonance contributions by the corresponding substituents) and n_{RO}, n_{Ar}, n_{O^-}, and n_{ArO} are the numbers of substituents RO (R = H, Alk), *p*- or *m*-XC_6H_4, O^-, and *p*-XC_6H_4O respectively. Such allowance for the resonance component is based on the hypothesis, made in analysing the σ^{ph} constants[48], that substituents capable of conjugation and of the same structural type make a constant resonance contribution§.

It was assumed[49] for all *p*- or *m*-XC_6H_4 groups that $E_S = 0$. Since this postulate is arbitrary[72], the inclusion of arylphosphinic and arylphosphonic acids in the general set with other

§ This procedure for isolating the resonance contribution was adopted also because experimental data[71] for phosphinic acids containing substituents incapable of conjugation were insufficient for the construction of a reliable regression.

acids may lead to errors in the estimated regression of coefficients. Consequently regression No.1 must be regarded as basic in Table 2. The agreement between the estimated coefficients in regressions 1 and 3 and the quite high statistical indices of the latter indicate that the postulated equality of the steric constants of methyl and aryl groups produces no appreciable errors. Disregard of the electrostatic correction increases the resonance contribution of the O^- substituent by this amount, while the remaining regression coefficients remain unchanged (cf. regressions 1 and 2).

Thus use of the constants σ^* and E_s respectively to characterise inductive and steric effects of substituents enables Eqn.(9) to provide a good description of pK_a values for phosphinic acids, pK_{a1} and pK_{a2} for phosphonic acids, and the three values for phosphoric acid. The range of variation in acid strength covered by this equation is 12 lg units: i.e. the relative precision of the description $S = 1.4\%$. The results in Table 2 indicate that substituents destabilise by an inductive mechanism ($a_1 < 0$), and stabilise by a conjugation mechanism ($a_4 - a_7 > 0$), the initial state in the dissociation of organic acids of phosphorus. The difference $\Delta\sigma^*_{rc}$ (Section II) calculated from $a_1 = -\alpha^*\Delta\sigma^*_{rc}/2.303RT$ (see Eqn.4) is 0.66. The corresponding value for the dissociation of aliphatic carboxylic acids (in water at 25 °C) is 0.77.[25] Since $\sigma^*(CH_3POOH) = 1.47$, we obtain $\sigma^*(CH_3POO^-) = 0.81$, whereas $\sigma^*(COOH) = 1.7$ and $\sigma^*(COO^-) = 0.93$.[25] Hence for the dissociation of organic acids of phosphorus and of aliphatic carboxylic acids not only are the $\Delta\sigma^*_{rc}$ values closely similar but also the inductive constants of initial and final states respectively of their reaction centres.

The statistical significance of the coefficient a_3 in Eqn.(9) indicates different intensities of steric interaction of the substituents X, Y with the fragment $\rangle$POOH and with the corresponding anion. The sign of a_3 shows that the acid becomes weaker as the steric effects of the substituents become greater. This can be explained by steric hindrance to solvation stabilisation of the anion by X and Y, as occurs in the dissociation of carboxylic acids containing bulky substituents[73-75]. Significant steric influence of substituents on the strengths of XYPOOH acids is demonstrated by the regression[54]

$$pK_{a_2}(XP(O)(OH)_2) = (7.987 \pm 0.048) - (1.345 \pm 0.037)\sigma^* - (0.210 \pm 0.046)E_s$$
$$n=6;\ R=0.9987;\ S_0=0.073 \qquad (10)$$

obtained for very accurate measurements[76] of pK_{a2} for six phosphonic acids containing substituents incapable of conjugation. The independent term coincides with the experimental value[76] of $pK_{a2}(CH_3PO(OH)_2)$, and estimates of the coefficients for inductive and steric contributions agree well with the corresponding estimates in the regression in Table 2. Exclusion of the steric contribution from regression (10) produces a sharp impairment of its statistical indices[54] (for example, the standard deviation is doubled).

V. NON-ADDITIVITY OF EFFECTS OF SUBSTITUENTS ATTACHED TO A FOUR-COORDINATED PHOSPHORUS ATOM

Equation (4) contains a cross term, a contribution proportional to the product of the inductive constants of the substituents. The presence of cross terms is implied by the general form of polylinear equations[1,27], and is interpreted as a change in the intensity of the effect of one factor under the influence of another factor. These non-additive effects are closely connected with the phenomenon of isoparametricity[1,77,78], and have now been shown for various pairs of factors (medium and structure, pressure and structure, reactant and substrate structures, etc.) in many organic reactions[1,77-89]. A well known example of such non-additivity is the dependence of activation energy on reactant structure[1,12,77,89]. The character of the combined influence of different factors is obviously determined by the detailed mechanism of the chemical process[1,27,77].

The statistical significance of a_2 in the regressions in Table 2 presupposes non-additivity of the inductive effects of substituents X and Y on the dissociation of XYPOOH acids. However, exclusion of the cross term from these regressions neither impairs appreciably the quality of the description nor changes the estimated coefficients a_0, a_1, and a_3–a_7.[49] The variables $\Sigma\sigma^*$, $\sigma^*_X\sigma^*_Y$, and ΣE_s in the regressions are strongly interdependent (non-orthogonal). Because of the many-sided interrelationship the estimate of one coefficient (e.g. a_2) may be shifted relative to its true value without appreciably displacing the estimates of other coefficients.

The non-orthogonality of the scales of constants representing the abilities of substituents (or solvents) to undergo various types of interaction is a common weak point in multidimensional correlation analysis, to which many investigators do not pay due attention. A frequent consequence of such non-orthogonality is that the absolute estimates of regression coefficients obtained by least squares lose their physical content and in general cannot be compared either within a single regression or with corresponding parameters in analogous equations for other processes.

There are in principle two possible escapes from such a situation—(i) rejection of the convenient method of least squares and (ii) preliminary factorisation of the variables—both unattractive for correlation analysis[90]. The latter procedure, which is widely used in experiment design, leads to variables losing their concrete meaning (physical or quasi-physical), and furthermore does not permit the construction of invariant scales of constants for substituents (or solvents). In the Reviewers' opinion, therefore, the most acceptable way at present is first to deduce various equations based on some *a priori* considerations (theoretical or formal), followed by logical analysis of the parameters in regression corresponding to these equations, in terms of the meaning that had been implied *a priori* in these parameters. In some cases a model calculation may prove very useful: coefficients therein are specified that are close to those in the regression obtained, values of the function to be correlated are then calculated from these coefficients and the corresponding set of variables, and these values are "coarsened" (errors close to those in the experimental data are introduced). After this the coefficients in the regression are found from the resulting values of the function and the original set of variables. Comparison of the results with the specified coefficients will indicate whether the correctibility of the variables will lead in a given case to displacement of the estimated coefficients.

A model calculation[49] made to test the displaceability of the estimated coefficient a_2 in the regressions in Table 2 indicates that with a given set of variables, even when the cross term is *a priori* significant, its exclusion leads to no significant deterioration in the quality of the description and to no displacement of the estimates of other coefficients in the regression. Thus there is no direct confirmation of the presence of a cross term in Eqn.(4).

Little information is available on non-additive effects of substituents attached to four-coordinated phosphorus. Thus non-additivity was shown[91] in the influence of two alkoxy-groups X and Y on the alkaline hydrolysis of the esters $XYPOOC_6H_4NO_2$-*p*, but a recent analysis[92] of a larger number of results has indicated complete additivity. This example illustrates how changing the set of substituents and using

experimental results from different sources can influence the apparent character of the combined effects of substituents in a reaction series. In the Reviewers' opinion a solution to this problem should be based in each particular case on detailed analysis of the parameters of the correlation model for the given process, and it is desirable that self-consistent data should be used to deduce this model.

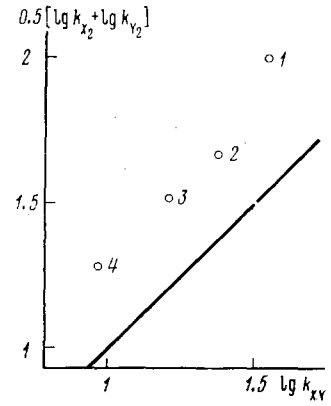


Figure 2. Non-observance[55] of additivity test for effects of substituents in alkaline hydrolysis of X(C_2H_5)POF, with X: 1) CH_3O; 2) C_2H_5O; 3) n-C_3H_7O; 4) iso-C_3H_7O.

Table 3. Coefficients and statistical criteria of Eqn.(11)*[53].

Coeff. or statistical criterion	№ 1	№ 2	№ 3
a_0	3.317±0.072	3.037±0.098	3.372±0.082
a_1	2.131±0.218	2.350±0.442	2.549±0.172
a_2	0.196±0.032	—	0.211±0.037
a_3	0.175±0.069	0.160±0.143	—
a_4	−5.085±0.394	−5.100±0.761	−5.868±0.295
n	18	18	18
R	0.9971	0.9866	0.9957
S_0	0.069	0.155	0.083

*The compounds used are given in Ref.53.

A clear example of non-additivity of the effects of *P*-substituents is alkaline hydrolysis of the acid fluorides XYPOF, for which the criterion of additivity[55] is not observed: i.e. experimental points for the plot of lg k(XYPOF) against 0.5[lg k(X_2POF) + lg k(Y_2POF)] do not lie on a straight line of unit slope passing through the origin (Fig.2). The rate of this reaction (in water at 25 °C) [93] is well described (Table 3) by the non-additive equation[53]

$$\lg k(\mathrm{XYP(O)F}) = a_0 + a_1 \sum \sigma^* + a_2 \sigma^*_X \sigma^*_Y + a_3 \sum E_s + a_4 n_{RO} \qquad (11)$$

in which a_4 is the resonance contribution by the RO substituents and n_{RO} the number of such substituents in the molecule. Omission of the cross term $a_2\sigma^*_X\sigma^*_Y$ impairs the quality of the description (regression 2 in Table 3).

The contribution by non-additive interaction of the substituents is small when X and Y are alkyl, and amounts to 0.3 to 0.4 lg unit when they are alkoxyl groups. Alkaline hydrolysis of the acid fluorides XYPOF is obviously greatly hindered by the resonance effect of the alkoxy-groups, which stabilises the initial state. It is curious that this resonance effect in this reaction series is largely balanced by the inductive effect of these groups. Omission of the contribution $a_3\Sigma E_S$ also somewhat impairs the quality of the description: i.e. reactivity in the series is influenced by spatial factors, for steric effects of substituents X and Y hinder the reaction, by destabilising the transition state. Despite the smallness of the coefficient a_3 (Table 3), the steric contribution to lg k may be considerable: thus for the compound (iso-$C_3H_7O)_2$POF it is 0.33 lg unit, but the corresponding value when X = Y = t-C_4H_9O should be 0.61.

Confirmation of the non-additive character of the influence of substituents on the rate of substitution of fluorine in the compounds XYPOF can be obtained also by direct application of the principle of polylinearity[1], according to which the rate should be given by

$$\lg k(\mathrm{XYP(O)F}) = a_0 + X' + a_1 Y' + a_2 X'Y', \qquad (12)$$

if the effects are defined as

$$X' = \lg k(\mathrm{X_tY_0P(O)F}) - \lg k(\mathrm{X_0Y_0P(O)F});$$
$$Y' = \lg k(\mathrm{X_0Y_tP(O)F}) - \lg k(\mathrm{X_0Y_0P(O)F}),$$

where lg k(X_0Y_0POF) relates to the compound containing substituents X_0 and Y_0 chosen as standard. The principle imposes on the coefficients in (12) the limitations[1,27] a_0 = lg k(X_0Y_0POF) and a_1 = 1. The use of such scales to analyse the real significance of the coefficient a_2 in Eqn.(12) is extremely convenient, since mathematical expectancies are available for all the other coefficients. This prevents the appearance of a significant cross term because of shifts in the estimates of a_0 and a_1, e.g. owing to non-orthogonality of the variables X', Y', and $X'Y'$, in cases in which the effects of the factors are actually additive. Furthermore, use of the X' and Y' scales enables the presence to be revealed of small cross terms, whose omission does not affect significantly the statistical indices but leads to displaced estimates of a_0 and a_1. Choice of X_0 = Y_0 = C_2H_5 and calculation of X' and Y' for various groups X and Y gave[53] values of lg k for alkaline hydrolysis of compounds XYPOF well described by Eqn.(12) with a statistically significant cross term $a_2X'Y'$, exhibiting good convergence of estimates of a_0 and a_1 with the theoretical coefficients.

The structural effects of the departing aryloxy-group and the nucleophile on the rate of reaction of 2-aryloxy-2-oxo-1,3,2-dioxaphosphorinans with various nucleophilic reagents are also significantly non-additive[83]. A bimolecular mechanism of direct substitution S_N2(P) is involved[83], so that departing group and attacking nucleophile should interact strongly in the transition state. Thus the effects of two substituents attached to a phosphorus atom may indeed be non-additive. Such non-additivity has been confirmed in a study of alkaline hydrolysis of the esters XYPSOC_6H_4X-*p*(*m*).[94]

VI. COMPARISON OF INFLUENCE OF STRUCTURAL FACTORS ON DISSOCIATION OF XYPOOH AND XCOOH ACIDS

It is generally accepted in organophosphorus chemistry[95,96] that the electronic effects of substituents on reaction centres involving phosphorus and carbon atoms—including phosphinico and carboxyl—are different in nature. It has been shown above that substituents X and Y influence the strengths of

XYPOOH acids mainly by inductive and resonance mechanisms. The constant of sensitivity to the inductive effect for this series $\rho_P^* = 1.358 \pm 0.040$ (Table 2) is close to the corresponding value $\rho_C^* = 1.809 \pm 0.028$ for the dissociation of XCOOH acids[25].

Table 4. Resonance contributions ΔpK_P and ΔpK_C by substituents to pK_a (in water at 25 °C) of XYPOOH and XCOOH.[51]

X	ΔpK_P^* (F) **	ΔpK_C
OH	1.221±0.084 (51)	1.74
O^-	3.160±0.041 (40)	3.98
O^-	4.486±0.041 (40)	5.25***
Ph	0.256±0.041 (20)	0.57
R****	0.00	0.00

*Values taken from regressions in Table 2.
**F = number of degrees of freedom.
***Without electrostatic correction.
****Here R = CH_3 and other substituents incapable of conjugation.

Table 4 lists the resonance contributions ΔpK_P made by phenyl, hydroxyl, and oxide substituents (with and without the electrostatic correction) to the pK_a values of XYPOOH acids and the corresponding contributions ΔpK_C made by them¶ to the pK_a values of XCOOH acids, the latter calculated by means of the equation[1]

$$\Delta pK_C = pK_a(XCOOH) - 4.748 + 1.809\sigma^*.$$

Comparison was impossible withother substituents capable of conjugation, for either experimental data for such carboxylic acids were lacking or the pK_a values available for the corresponding organic acids of phosphorus were unreliable. Fig.3 shows a linear relation between ΔpK_C and ΔpK_P. The corresponding regression[51]

$$\Delta pK_C = (1.29 \pm 0.05)\Delta pK_P;\ r = 0.9976;\ s_0 = 0.18$$

passes through the origin, i.e. through the point X = Y = CH_3. Such a relation indicates that the effects of these substituents on the pK_a values of phosphororganic and carboxylic acids are identical in nature. The ratio of ΔpK_C to ΔpK_P is given by the slope of the straight line in Fig.3, which coincides with the ratio $\rho_C^*/\rho_P^* = 1.37 \pm 0.04$: i.e. the ratio of the resonance contributions in the dissociation of XCOOH and XYPOOH acids is equal to that of the corresponding inductive contributions. Hence it follows by proportion that the ratio of inductive and resonance contributions to the overall effect of a substituent is the same in the series under comparison.

The reaction centres COOH and POOH are of the $-C$ type, so that a correlation should be observed between the conjugation contributions ΔpK_C (ΔpK_P) and the constants $\sigma_{res}^+ = \sigma^+ - \sigma^0$ for the $+C$-type substituents C_6H_5, OH, and O^-. A very good linear relation does indeed exist[51] between ΔpK_C and σ_{res}^+, passing through the origin, i.e. through the point for the methyl substituent (Fig.4):

$$\Delta pK_C = (-2.209 \pm 0.003)\sigma_{res}^+;\ r = 0.9999;\ s_0 = 0.005.$$

The point for the resonance contribution of the substituent O^- without the electrostatic correction does not lie on the line. This demonstrates unambiguously the necessity for such correction in the case of charged substituents capable of conjugating with the reaction centre†.

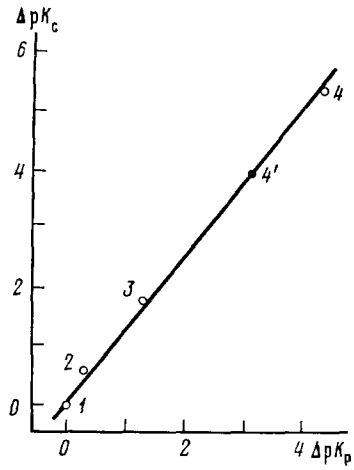


Figure 3. Relation[51] between resonance contributions to pK_a of carboxylic and organophosphorus acids (ΔpK_C and ΔpK_P) by the substituents: 1) CH_3; 2) C_6H_5; 3) HO; 4) O^-; 4') as (4) with electrostatic correction.

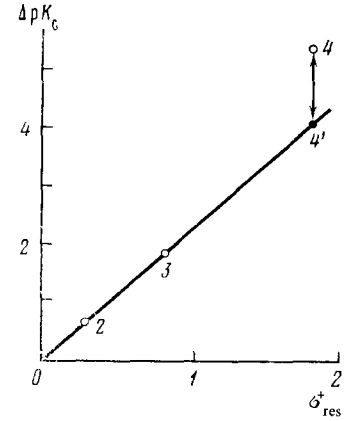


Figure 4. Correlation[51] between resonance contributions ΔpK_C and σ_{res}^+ constants: numbering as in Fig.3.

¶ The electrostatic correction ΔpK_{a1} for pK_{a2} of carbonic acid was calculated[51] from the geometry of the carbonate anion CO_3^{2-}, by a procedure similar to that adopted for phosphonic acids and phosphoric acid.

† The need to allow for electrostatic interaction has been shown[1,25] for charged substituents incapable of conjugation with the reaction centre.

Thus the electrostatically and statistically corrected pK_a values of XYPOOH acids are described by the equation[51]

$$pK_a(XYP(O)OH) = pK_a(Me_2P(O)OH) + \rho_P^* \sum \sigma^* + a_1\sigma_X^*\sigma_Y^* + \rho_{res\,P}^+ \sum \sigma_{res}^+ \quad (13)$$

and the pK_a values of XCOOH acids by[51]

$$pK_a(XCOOH) = pK_a(MeCOOH) + \rho_C^*\sigma^* + \rho_{res\,C}^+\sigma_{res}^+ \quad (14)$$

where $\sigma_{res,P}^+ = -1.709$ and $\sigma_{res,C}^+ = -2.209$ are the sensitivities of the series to the resonance influence of substituents. In these equations the ratio of the inductive contributions by substituents is equal to that of their resonance contributions:

$$\rho_P^*/\rho_C^* = \rho_{res\,P}^+/\rho_{res\,C}^+ = \alpha = 0.760 \pm 0.028. \quad (15)$$

From this formula together with Eqns.(13) and (14) it necessarily follows for the pK_a of XYPOOH acids in which Y remains unchanged that

$$pK_a(XYP(O)OH) = A_Y + \alpha pK_a(XCOOH) + a\sigma_X^*\sigma_Y^* + \delta_P E_{s,X} \quad (16)$$

where

$$A_Y = pK_a(MeYP(O)OH) - \alpha pK_a(MeCOOH).$$

Hence with any substituent X and any given substituent Y the experimental pK_a values should obey (16) with statistically significant contributions $\delta_P E_{s,X}$ and $a\sigma_X^*\sigma_Y^*$.

Conformity to Eqn.(16) has been verified[52] for the pK_{a_1} and pK_{a_2} values (Y respectively OH and O^-) of substituted phosphonic acids, for which this equation becomes

$$pK_{a_1}(XP(O)(OH)_2) = A_{OH} + \alpha pK_a(XCOOH) + a\sigma_{OH}^*\sigma_X^* + \delta_P E_s \quad (16a)$$

$$pK_{a_2}(XP(O)(OH)_2) = A_{O^-} + \alpha pK_a(XCOOH) + \delta_P E_{s,X}. \quad (16b)$$

The contribution $a\sigma_X^*\sigma_{O^-}^*$ is absent from the latter formula, since $\sigma_{O^-}^* = 0$.[26,49] Mathematical expectancies are known for all the coefficients in (16a) and (16b): δ_P and a should not differ significantly from -0.230 ± 0.027 and 0.161 ± 0.042 respectively (Table 2); from experimental values of pK_{a_1}. $.(CH_3PO(OH)_2)$, $pK_{a_2}(CH_3PO(OH)_2)$, and $pK_a(CH_3COOH)$ it has been found[52] that $A_{OH} = -0.93 \pm 0.147$ and $A_{O^-} = 2.71 \pm 0.147$, while $\alpha = 0.760 \pm 0.028$.

Checking the validity of Eqns.(16a) and (16b) reveals poor statistical indices (Table 5) only for the dependence of pK_{a_1} and pK_{a_2} (regressions 1 and 3 respectively) of phosphonic acids on the pK_a of the corresponding carboxylic acids.

Inclusion of the terms $a\sigma_{OH}^*\sigma_X^*$ and $\delta_P E_S$ in pK_{a_1} and of $\delta_P E_S$ in pK_{a_2} (regressions 2 and 4) sharply improves the quality of the description. The estimates of A_{OH}, A_{O^-}, and α agree well with the values expected mathematically; the estimates of δ_P and a have the required signs and also agree satisfactorily with their theoretical values (above). Consequently the pK_a of corresponding phosphonic and carboxylic acids are indeed represented by the above relations.

It is evident also from formulae (16a) and (16b) and the corresponding regressions that the pK_{a_1} and pK_{a_2} values of phosphonic acids should be given by the single equation[52]

$$pK_{a_{1(2)}}(XP(O)(OH)_2) = A_{OH} + \beta T + \alpha pK_a(XCOOH) + a\sigma_{OH}^*\sigma_X^* + \delta_P E_s \quad (17)$$

in which T is respectively 0 and 1. Here $\beta = -3.64 \pm 0.071$ is the difference between the independent terms in regressions 2 and 4 (Table 5).

The graphical illustration of Eqn.(17) in Fig.5 shows that the large majority of points lie close to a straight line of slope α. It is interesting that the pK_{a_2} values for trifluoro- and trichloro-methylphosphonic acids are located closest to the regression line if negative pK_a values are used for the corresponding carboxylic acids[72], whereas points corresponding to the pK_{a_1} of the above acids depart considerably from the straight line whatever the pK_a values of trifluoro- and trichloro-acetic acids. The pK_{a_1} values of the two phosphonic acids deviate also from the regressions in Table 2, apparently because they had been determined incorrectly.

Equation (17) corresponds to regression 5 in Table 5, covering 41 pK_a values for 22 phosphonic acids. All its coefficients agree well with the corresponding coefficients of regressions 2 and 4 and with their theoretical values. The statistical indices of the regression are good.

Thus the good adherence to relations (16a), (16b), and (17) for acids containing diverse substituents X, including charged groups (O^-) and those capable of conjugation with reaction centres, finally confirms the correctness of Eqns. (13)–(15). This indicates that the structural effects of substituents on the strengths of XYPOOH and XCOOH acids are entirely of the same type.

VII. CONCLUSION

Among the results covered in the Review the most unexpected to the Reviewers is the good linear relationship between the contributions by the conjugation of substituents with POOH and COOH reaction centres, as well as the closely similar relations between inductive and resonance contributions to the overall effect of substituents for dissociation of the two series of acids XYPOOH and XCOOH. However, an analogous conclusion follows logically from the good correlation observed in 1953 [4] between the pK_a values of arylphosphonic acids and the Hammett σ-constants. The linear

Table 5. Coefficients and statistical criteria of relations (16a), (16b), and (17) between pK_{a_1} and pK_{a_2} values of phosphonic and carboxylic acids $XPO(OH)_2$ and XCOOH*[52].

Eqn.	Regression	A_Y	α	δ_P	a	β	n	R	S_0
(16a)	1	−0.310±0.251	0.670±0.055	—	—	—	21	0.9419	0.337
(16a)	2	−1.189±0.176	0.809±0.034	−0.327±0.045	0.319±0.057	—	21	0.9915	0.139
(16b)	3	2.768±0.271	0.799±0.059	—	—	—	21	0.9517	0.364
(16b)	4	2.528±0.154	0.804±0.033	−0.419±0.063	—	—	21	0.9871	0.199
(17)	5	−1.196±0.0116	0.805±0.021	−0.363±0.036	0.320±0.052	−3.805±0.055	41	0.9976	0.159

*Regressions were calculated from statistically and electrostatically corrected pK_a values for the acids $XPO(OH)_2$ (see reviews[49,52]) and XCOOH (compilation[52]).

dependence of ΔpK_P on ΔpK_C, which moreover passes through the origin, indicates either absence of any specific interactions of the substituents with the POOH fragment (e.g. involving *d*-orbitals of the phosphorus atom) or complete proportionality of the contribution by such interactions to the resonance contribution (which is described by the "carbon" constants σ_{res}^{+}) and (or) to the inductive contribution.

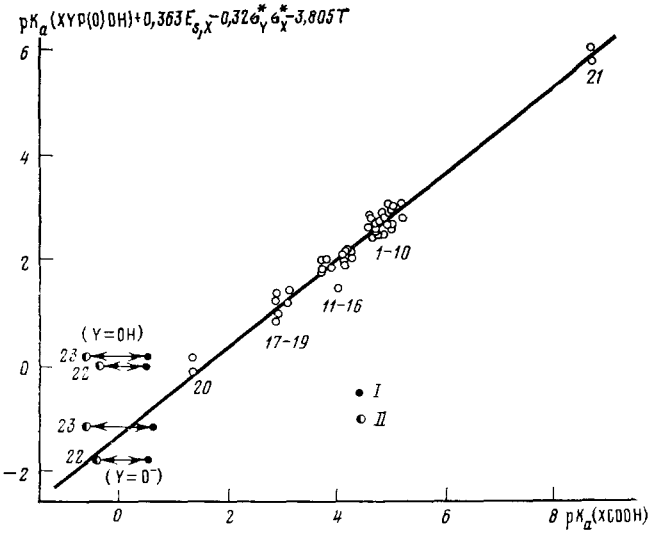


Figure 5. Graphical illustration of relation (17) [52] between the statistically and electrostatically corrected pK_{a_1} and pK_{a_2} values (Y = OH and O^-) of phosphonic acids XYPOOH and the pK_a values of carboxylic acids XCOOH, with X: 1) $n\text{-}C_3H_7$; 2) CH_3; 3) C_2H_5; 4) $iso\text{-}C_3H_7$; 5) $s\text{-}C_4H_9$; 6) $t\text{-}C_4H_9$; 7) $iso\text{-}C_4H_9$; 8) $n\text{-}C_4H_9$; 9) $t\text{-}C_5H_{11}$; 10) $(CH_3)_3.SiCH_2$; 11) $C_6H_5CH_2$; 12) $HOCH_2$; 13) C_6H_5; 14) HO; 15) $BrCH_2CH_2$; 16) H; 17) $ClCH_2$; 18) $BrCH_2$; 19) ICH_2; 20) Cl_2CH; 21) O^-; 22) F_3C; 23) Cl_3C; I) with $pK_a > 0$ for the acids CF_3COOH and CCl_3COOH; II) $pK_a < 0$ for these acids.

The steric effect exerted[47-54] by substituents X and Y on the strengths of XYPOOH acids cannot be regarded as an artefact, since the magnitude of the sensitivity coefficient δ is very stable: it depends neither on the size of the sample nor on the specific form of the equation. Exclusion of the steric contribution always impairs the accuracy of the description of experimental data, which is shown especially clearly by recent self-consistent values[76] for the pK_{a_2} of several phosphonic acids.

It is noteworthy that the steric contribution to the pK_a of XYPOOH acids may be considerable despite the small sensitivity coefficient δ to this type of interaction. The reason is the large absolute magnitudes of the constants E_s for bulky substituents[97]. The appearance of a steric contribution is obviously due not to steric hindrance by substituents to detachment of a proton but to their destabilisation of the anion by causing steric hindrance to formation of its solvation sheath. The view that substituents cause significant steric hindrance to solvation of carboxylate anions was expressed many years ago[98,75] and is supported by recent data[99,100].

Thus the results presented in this Review are evidence firstly of the adequacy of the list of types of intramolecular interaction used and of the satisfactory applicability of the mathematical models of the individual types of interaction using the "carbon" constants σ^*, E_s, and σ_{res}^{+} to represent the influence of substituents on the properties of four-coordinated quinquevalent phosphorus compounds, and secondly that the mathematical models of interactions (inductive, steric, resonance) and the corresponding substituent constants do indeed contain chemical and physical meaning axiomatically "incorporated" in them. Furthermore, the results of a recent series of studies[47-54] yet again confirm the objective character and a definite universality of the axiomatics of correlation analysis. Its limits of applicability in describing the influence of *P*-substituents on various properties of organophosphorus compounds are apparently determined by the general limits of applicability of the polylinearity principle[1,27] to these properties.

Analysis shows that the σ^{ph} constants widely used in organophosphorus chemistry are composite, comprising contributions by inductive, steric, and resonance effects of substituents#. The good description of diverse properties of organophosphorus compounds provided by these constants indicates that in many of their reaction series the relative contributions by individual interaction mechanisms to the overall effect of a *P*-substituent are about the same as in the dissociation of XYPOOH acids. Hence it is obvious that these constants are inapplicable only in reaction series in which the relative contributions differ markedly from those "incorporated" in these constants.

The σ^{ph} constants secure on important virtue—simplicity of the correlation equations—despite their complicated nature. In the Reviewers' opinion, therefore, they should be used as before to describe those reaction series to which they are readily applicable, provided comparison of organophosphorus reaction series with other series is not involved.

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α-Alkoxy-compounds of Phosphorus and Some of Their Analogues

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Data on the methods of synthesis of α-alkoxyalkyl derivatives of organophosphorus compounds are presented and their chemical properties and principal applications are examined.
The bibliography includes 305 references.

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I. INTRODUCTION

The α-alkoxyalkyl derivatives belong to the large class of derivatives of organophosphorus compounds with functional group substituents, which have been vigorously investigated in recent years. Novel and convenient methods of synthesis have been proposed for these compounds and certain practical applications have been discovered. However, there are no reviews in the Soviet and foreign literature devoted to the chemistry of these compounds, which was the reason why the present review was undertaken.

II. METHODS OF SYNTHESIS

α-Alkoxyalkyl derivatives of organophosphorus compounds are synthesised by several procedures which can be divided into two groups. The first group includes methods involving the α-alkoxyalkylation of tervalent phosphorus compounds, while the second comprises methods in which various groups in organophosphorus compounds are converted into α-alkoxy-groups.

1. α-Alkoxylation of Tervalent Phosphorus Compounds

(a) Alkylation of the Fully Esterified Tervalent Phosphorus Acids by α-Halogenoalkyl Ethers

The esters of α-alkoxyalkylphosphonic[1-26] and alkyl(aryl)-phosphinic[24,27,28] acids, including compounds containing various functional groups in the hydrocarbon substituents, are obtained by this method:

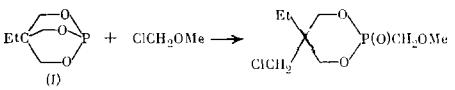
$$R^1P(OR^3)_2 + XCH(R^3)OR^4 \xrightarrow[-R^3X]{\Delta} R^1(R^3O)P(O)CH(R^3)OR^4 ,$$

where R^1 is a C_1-C_4 alkoxy-group, including one containing a halogen, OCH_2CH_2OMe, OCH_2CH_2OEt, OC_6H_4Y, Me, Et, Ph, or ClC_6H_4, Y = Cl, NO_2, CN, or Me_2NSO_2, R^2 = a C_1-C_5 alkyl group, including one containing a halogen, R^3 = H, C_1-C_7 alkyl, Ph, CH_2Br, COMe, COOMe, COOEt, $CONH_2$, CONHEt, CON⟨⟩O, or $P(O)(OBu)_2$, R^4 = C_1-C_{18} alkyl, $(CH_2)_n$–Ph, $ZCH{=}CHCH_2$, or $ZCH{=}CHCH_2CH_2$ (n = 0, 1, or 2 and Z = H, Cl, Br, or C_1-C_5 alkyl), R^3R^4 = $-OCH_2CH_2-$, $(CH_2)_m$ (m = 3 or 4) $-O-C_6H_3Cl$, or $-CH_2CH_2-C_6H_4$, and X = Cl or Br.

4,5-Unsubstituted and monosubstituted 2-alkoxy(diethylamino)-1,3,2-dioxaphospholans[29-34] and the bicyclic phosphite (I) [35] react with ring opening:

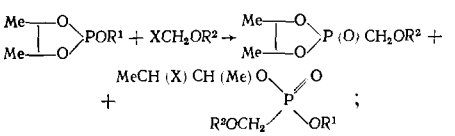
$$R^1\text{-}C_2H_3O_2P^3 + XCH_2OR^3 \rightarrow XCH_2CH(R^1)O(R^2)P(O)CH_2OR^3$$

R^1 = H, Me; R^2 = NEt_2, OEt, OCH_2CH_2Y, Y = Cl, F, OEt;
R^3 = C_1-C_4 alkyl; X = Cl, Br, I



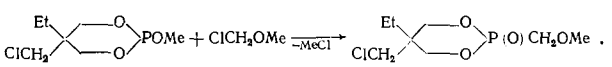
(I)

2-Alkoxy-4,5-dimethyl-1,3,2-dioxaphospholans interact with alkyl chloromethyl ethers to form a mixture of two substances[31]:



R^1 = Et, CH_2CH_2Cl; R^2 = C_1-C_4 alkyl; X = Cl, Br .

The reaction of 5-chloromethyl-5-ethyl-2-methoxy-1,3,2-dioxaphosphorinane with chloromethyl methyl ether proceeds with retention of the ring[34].



The methoxymethylation of tetraethyl methoxycarbonylmethylenediphosphonite is accompanied by the keto–enol migration of the ethoxy(methoxymethyl)phosphinyl group[36,37]:

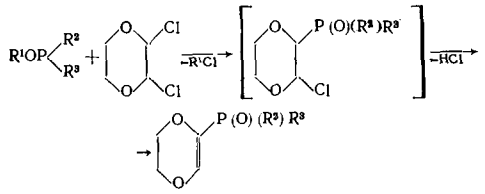
$$[(EtO)_2P]_2CHCOOMe + 2MeOCH_2Cl \xrightarrow[-2EtCl]{} EtO(MeOCH_2)P(O)CH{=}C(OMe)OP(O)(OEt)CH_2Me .$$

The alkylation of triethylphosphite with bishalogenodimethyl ethers yielded the corresponding diphosphonate[38]:

$$2(EtO)_3P + XCH_2OCH_2X \xrightarrow[-2EtCl]{} (EtO)_2P(O)CH_2OCH_2P(O)(OEt)_2 ;$$
X = Cl, Br .

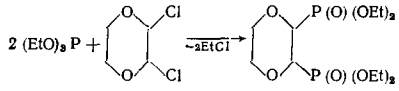
In the interaction of 2,3-dichloro-1,4-dioxan with 1 mole of trialkyl phosphite, phosphonite, or phosphinite the alkylation

product undergoes spontaneous dehydrochlorination[39,40]:

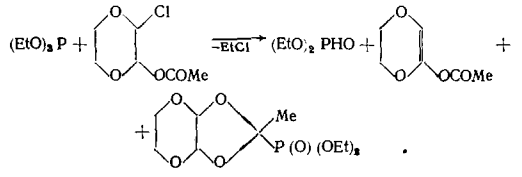


$R^1 = C_2—C_4$ alkyl; R^2, $R^3 = OR^1$, Et, Ph, ClC_6H_4 .

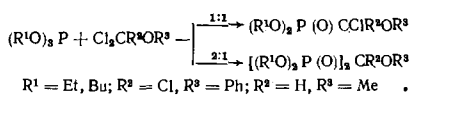
The reaction of 2,3-dichloro-1,4-dioxan with an excess of triethyl phosphite leads to 2,3-bis(diethoxyphosphinyl)-1,4-dioxan[5]:



The interaction of triethyl phosphite with 3-acetoxy-2-chloro-1,4-dioxan leads to a mixture of products[41]:

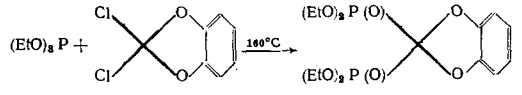


Mainly one or two chlorine atoms, depending on the reaction ratio, are substituted preferentially in trichloromethyl phenyl and dichloromethyl methyl ethers when these interact with trialkyl phosphites[9,26]:

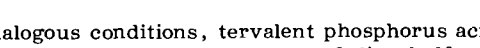


$R^1 = Et, Bu$; $R^2 = Cl$, $R^3 = Ph$; $R^2 = H$, $R^3 = Me$.

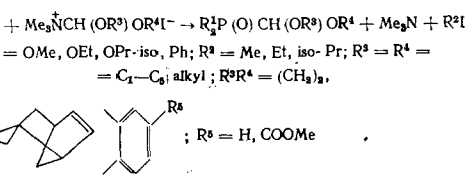
Bisphosphorylated benzodioxole has been obtained by the reaction of 2,2-di-chloro-benzo[*d*]dioxole with an excess of triethyl phosphite[5]:



When ethoxymethyltrimethylammonium chloride is used instead of α-chloroethers, the alkoxylation reaction proceeds only under severe conditions[42]:



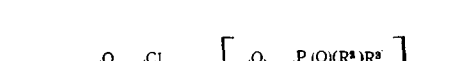
Under analogous conditions, tervalent phosphorus acid esters are alkylated by the methoiodides of dimethylformamide acetals[43,44]:



$R^1 = OMe, OEt, OPr\text{-}iso, Ph$; $R^2 = Me, Et, iso\text{-}Pr$; $R^3 = R^4 =$ $= C_1—C_6$ alkyl; $R^3R^4 = (CH_2)_5$,

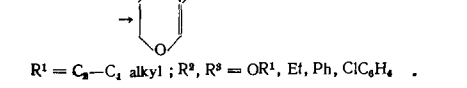
; $R^5 = H, COOMe$.

When alkyl phosphoroisocyanatidites are alkylated, the completion of the reaction requires prolonged refluxing of the mixture or the presence of a catalyst ($FeCl_3$):[45–47]



$n = 1, 2$; R^1, $R^2 = Me, Et$; $R^3 = H, Cl, CCl_3, MeOC(O), EtOC(O)$.

Alkylation of the ethyl ester of diphenylphosphinothious acid is complicated by oxidation-reduction processes and leads to a mixture of products[48]:



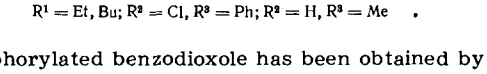
$R^1 = H, Me$; $R^2 = C_1—C_4$ alkyl.

(b) Alkylation of Ester-Chlorides of Tervalent Phosphorus Acids

By virtue of the ready heterolysis of the carbon–halogen bond, α-halogenoethers are some of the most reactive alkylating agents. However, in the reactions with highly nucleophilic derivatives of tervalent phosphorus considered above this feature of the chemical properties of α-halogenoethers is manifested only by some acceleration of the alkylation reaction or by its occurrence under milder conditions, compared with those required, for example, by alkyl halides.

The situation is different when the less nucleophilic ester-halides of tervalent phosphorus acids are used in the alkylation reactions; whereas the latter are only sluggishly alkylated by alkyl halides or not at all, they are capable of reacting effectively with α-halogenoalkyl ethers via the Arbuzov reaction. Thus dialkyl halogenophosphites[49–53] and 2-chloro-1,3,2-dioxaphospholans[31–33,54,55] interact to form the ester-halides of alkoxyalkylphosphonic acids:

$R^1 = Et, Bu, Am$; $R^2 = H, Cl, Me, COOMe$; $R^3 = H, Cl$; $R^4 = Et, Bu$; $X = Cl, F$

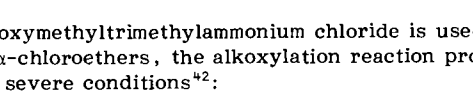


$R^1 = H, Me$; $R^2 = H, Cl$; $R^3 = C_1—C_4$ alkyl; $X = Cl, Br$

The less nucleophilic alkyl phosphorodichloridites (difluoridites) are alkylated by α-chloroethers only in the presence of electrophilic catalysts—$FeCl_3$, $AlCl_3$, BF_3, etc.:[7,56–64]

$R^1 = Me, Bu$; $R^2 = C_1—C_4$ alkyl, $PhCH_2$, CH_2Cl; $R^3 = H, CCl_3, CO_2Me$; $R^4 = H, Cl$; $X = Cl, F$.

All the halogen atoms in bis-α-chloroethyl and α,α-di-iodoethyl methyl ethers are substitutes when the latter interact with methyl phosphorodichloridite[56]:



Together with alkyl phosphorodichloridites, acetyl phosphorochloridites or acetyl phosphonochloridites, obtained as intermediates when a mixture of ethyl(phenyl)dichlorophosphine or ethyl phosphorodichloridite and an α-chloro-ether is acted upon by acetic anhydride, also react with α-chloroalkyl ethers[64,65]:

$R = Et, Ph, OEt$

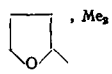
The chlorides of tervalent phosphorus acids and some of their derivatives also react with acetals and the orthoesters of carboxylic acids to form α-alkoxyalkyl derivatives of phosphorus. As a result of the exchange of the alkoxy-group between the acid chloride and the acetal or orthoester, α-chloroalkyl ethers and neutral esters or ester-chlorides of

tervalent phosphorus acids are formed initially and their interaction ultimately yields α-alkoxyalkyl compounds of phosphorus.

Phosphorus trichloride[67,68], alkyl phosphorodichloridites[68–70], diaryl phosphorochloridites[71,72], dialkyl phosphorochloridites[70–78], phenyldichlorophosphine[78,79], ethyldichlorophosphine and diethylaminoethylchlorophosphine[80], diethyl- and diphenyl-chlorophosphines[69,71,75,76,78,79,81], and aryl(alkyl) chlorophenylphosphonites[79] have been made to undergo this reaction:

$$R^1(R^2)PCl + R^3R^4C(OR^5)OR^6 \xrightarrow{-R^5Cl} R^1(R^2)P(O)CR^3R^4OR^5$$

$R^1 = Cl$, Et, Ph, OAlk, OAr; $R^2 = R^1$, NEt_2; $R^3 = H$, Me, OEt;

$R^4 = H$, Me, Et, Pr, Ph, CH_2CH_2OAlk,  , Me_2  $(Me)CH_2$—,

 ; $R^3R^4 = (CH_2)_5$; $R^5 = $ Alk, cyclo-C_6H_{11}, $CH_2CH{=}CH_2$,

CH_2CH_2OBu, CH_2CH_2Cl, CH_2CO_2Alk; $R^6 = R^5$, CH_2COAlk.

A mixture of trialkyl phosphite and phosphorus trichloride in proportions of 2 : 1 can be used in these reactions instead of dialkyl phosphorochloridites[20,72,75,82]. The interaction of phosphorus trichloride with three moles of an orthoester or an acetal[20,69,72–74,82–85] and also the reaction of alkyl(aryl) phosphorodichloridites[69,74,82] and phenyldichlorophosphine[69,78,79] with two moles of an acetal or an orthoester lead to the same products:

$$PCl_3 + 3R^1O(R^2O)CR^3R^4 \xrightarrow[-R^2Cl]{ZnCl_2} (R^2O)_2P(O)CR^3R^4OR^1 + 2ClCR^3R^4OR^1$$

$R^1 =$ Alk, $CH_2CH{=}CH_2$, CH_2CH_2Cl; $R^2 = R^1$, CH_2COOMe; $R^3 = H$, Me, Et; $R^4 = H, OR^1$

$$ROPCl_2 + 2CHR^1(OR^2)OR^3 \xrightarrow{-R^2Cl} RO(R^3O)P(O)CHR^1OR^3 + ClCHR^1OR^3$$

$R =$ Et, Bu, Ph; $R^1 = H$(Me, OEt; $R^2 =$ Et, Bu; $R^3 = R^2$, CH_2COOMe

$$PhPCl_2 + 2R^1CH(OR^2)OR^3 \xrightarrow{-R^2Cl} Ph(R^3O)P(O)CHR^1OR^2 + ClCHR^1OR^2$$

$R^1 = H$, Me, OEt, $R^2 =$ Alk, $CH_2{-}CH{=}CH_2$; $R^3 = R^2$, CH_2COOMe.

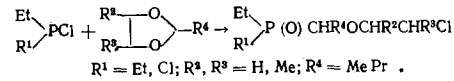
The reaction of phenyldichlorophosphine with methylal is accompanied by an oxidation-reduction process and leads to di(methoxymethyl)phenylphosphine oxide[79]:

$$2PhPCl_2 + 2(MeO)_2CH_2 \rightarrow PhP(O)(CH_2OMe)_2 + 2MeCl + PhPOCl_2.$$

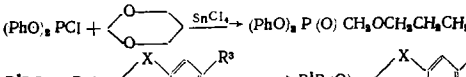
The interaction of dimethylformamide acetal with phosphorus trichloride leads to a mixture of products[86]:

$$PCl_3 + 3(MeO)_2CHNMe_2 \rightarrow [(MeO)_2P(O)]_2CHNMe_2 + (MeO)_3P + (MeO)_2P(O)CH(OMe)_2 + HCONMe_2 + Me_4\overset{+}{N}Cl^- + MeCl$$

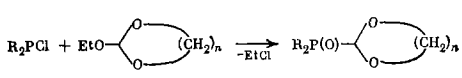
In the reactions of cyclic acetals with tervalent phosphorus acid halides the ring is opened[72,87,88], while in the reactions of cyclic orthoesters the ring is retained[78,89,90]:



$R^1 =$ Et, Cl; R^2, $R^3 = H$, Me; $R^4 =$ Me Pr.

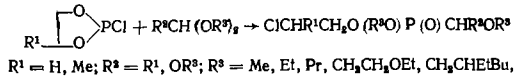


$R^1 =$ OEt, Ph; $R^2 =$ small alkyl; $R^3 = H$, OMe; X = O, S

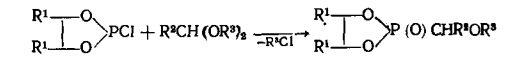


R = OEt, Ph; $n = 2, 3$.

The reactions of acetals and orthoesters with alkylene phosphorochloridites proceed both with ring opening[34,72,77,82,91] and with retention of the ring in the latter compounds[72,77]:

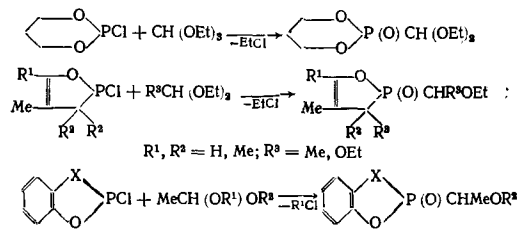


$R^1 = H$, Me; $R^2 = R^1$, OR^3; $R^3 =$ Me, Et, Pr, CH_2CH_2OEt, $CH_2CHEtBu$, $(CH_2)_nCl$, $n = 2, 4$;



R^1, $R^2 =$ Me, $R^3 =$ Me, Et, Pr; R^1, $R^2 = H$, $R^3 = CH_2{-}CH{=}CH_2$.

Propylene phosphorochloridite[78], chloro-oxaphospholens[92], o-phenylene phosphorochloridite, and salicyl phosphorochloridite[70,93] interact with acetals and an orthoester with retention of the ring:



R^1, $R^2 = H$, Me; $R^3 =$ Me, OEt

$R^1 =$ Me, Et; $R^2 =$ Et, CH_2COEt; X = O, COO.

Acyl phosphites[73], including those obtained by the reaction[94]

$$(EtO)_2POC(O)Me + HC(OEt)_3 \rightarrow (EtO)_2P(O)CH(OEt)_2 + MeC(O)OEt$$

$$PCl_3 + (RO)_2CHMe + (MeCO)_2O \rightarrow RO(Cl)P(O)CHMeOR + 2MeCOCl$$

R = Bu, Pr, Et,

interact with orthoesters similarly to phosphorochloridites.

The interaction of aryldichlorophosphines[95,96], alkyldichlorophosphines[97,98], and dialkyl phosphorochloridites[96,99,100] with acetalacylals proceeds with formation of a mixture of acid chlorides, ester-chlorides, ester-anhydrides, and acid esters of α-alkoxyethylarylphosphinic or α-alkoxyethylphosphonic acids. The interaction of dialkyl phosphorochloridites with an acetal-orthoformate also leads to a mixture of products[101].

(c) Alkylation of Chlorophosphines and Phosphoramidochloridites with α-Halogenoalkyl Ethers

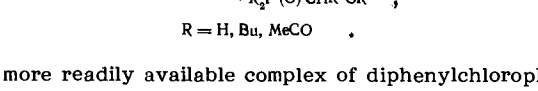
Under mild conditions, dialkyl(aryl)chlorophosphines are alkylated by α-halogenoalkyl esters[102–107]:

$$R^1_2PCl + R^2CHClOR^3 \rightarrow R^1_2(Cl)\overset{+}{P}CH(R^2)OR^3Cl^-;$$

(II)

$R^1 =$ Et, Ph, C_6H_4Me; $R^2 = H$, Me, CH_2Cl; $R^3 =$ small alkyl or halogenoalkyl.

When complex (II), which is stable at low temperatures, was treated with hydrogen sulphide, the corresponding phosphine sulphides were obtained[102–104], while treatment with water, aqueous alcohol, acetic acid, alcohol, or a pyridine–water mixture yielded phosphine oxides[102–106]:



R = H, Bu, MeCO.

The more readily available complex of diphenylchlorophosphine and aluminium chloride can be used in this reaction instead of free diphenylchlorophosphine[108,109].

Ethyl *N*,*N*-diethylphosphonamidochloridite reacts similarly with alkyl chloromethyl ethers in the cold, forming a complex whose decomposition with hydrogen sulphide or sulphur dioxide is accompanied by deamination[110–113]:

$$Et_2N(Et)PCl + ClCH_2OR \rightarrow Et_2N(Cl)\overset{+}{P}(Et)CH_2ORCl^- \rightarrow$$
$$\rightarrow \begin{cases} \xrightarrow{H_2S} Et(Cl)P(S)CH_2OR \\ \xrightarrow{SO_2} Et(Cl)P(O)CH_2OR \end{cases}$$
R = small alkyl.

Phosphorodiamidous chlorides are alkylated by alkyl halogenomethyl ethers also with formation of quasi-phosphonium salts, whose decomposition with hydrogen sulphide or alcohols in the presence of tertiary amines leads to the diamides of alkoxymethylphosphonothioic acids[114,115]; the decomposition of the phosphonium salts with alcohols in the absence of a hydrogen chloride acceptor leads to amidoesters, while decomposition with alcohols and hydrogen chloride results in the formation of the diesters of alkoxymethylphosphonic acids[113,115–117,119]:

$$(Et_2N)_2PCl + X\,CH_2OR \rightarrow (Et_2N)_2\overset{+}{P}(Cl)CH_2ORX^- \rightarrow$$
$$\rightarrow \begin{cases} \xrightarrow{Et_3N+H_2S} (Et_2N)_2P(S)CH_2OR \\ \xrightarrow{Et_3N+R^1OH} (Et_2N)_2P(O)CH_2OR \\ \xrightarrow{R^1OH} Et_2N(R^1O)P(O)CH_2OR \\ \xrightarrow{R^1OH+HCl} (R^1O)_2P(O)CH_2OR \end{cases}$$
R, R^1 = small alkyl; X = Cl, Br, I .

The complexes of aryldichlorophosphines and aluminium chloride readily interact with alkyl chloromethyl ethers; after the alcoholysis of the reaction products, the esters of alkoxymethylarylphosphinic acids were isolated[120]:

$$ArPCl_2 \cdot AlCl_3 + ROCH_2Cl \rightarrow [ROCH_2(Ar)\overset{+}{P}Cl_2][AlCl_4]^- \xrightarrow{R^1OH} \rightarrow ROCH_2(Ar)P(O)OR^1$$
Ar = Ph, $CH_3C_6H_4$; R, R^1 = small alkyl.

(d) Alkylation of Tervalent Phosphorus Acid Salts with α-halogenoalkyl Ethers

When sodium, potassium[1,9,16,21,38,40,121–124], or silver[125] dialkyl phosphites were heated at 100 °C with α-chloroalkyl ethers, the corresponding phosphonates and diphosphonates were obtained:

$$(R^1O)_2POM + XCH_2(OR^2)R^3 \rightarrow (R^1O)_2P(O)CHR^3OR^2 + MX \xrightarrow[-R^1X]{\Delta} \rightarrow MO(R^1O)P(O)CHR^3OR^2$$
$$2(R^1O)_2POM + XCH_2OCH_2X \rightarrow [(R^1O)_2P(O)CH_2]_2O + 2MX$$
R^1 = C_1–C_4 alkyl, CH_2CH_2OAlk, $CH_2CH{=}CH_2$, Ph; R^2 = C_1–C_4 alkyl, CH_2Ph; R^3 = H, P(O)$(OBu)_2$; R^2R^3 = $(CH_2)_4$, $-CHMe-CH_2CH_2CHCl-$;
X = Cl, Br, I; M = Na, K, Ag .

The reaction of sodium, potassium, and halogenomagnesium salts of phosphinous acids with alkyl chloromethyl ethers on refluxing in tetrahydrofuran results in the formation of the corresponding phosphine oxides[126–131]:

$$R^1_2POM + ClCH_2OR^2 \rightarrow R^1_2P(O)CH_2OR^2 + MCl$$
R^1 = Et, Bu, CH_2Ph; R^2 = C_1–C_{10} alkyl, $-CH_2-$  ,
CH_2CH_2OMe, $(CH_2CHR^3O)_nAlk$; R^3 = H, Me; n = 1, 3;
M = Na, K, MgBr .

The alkoxymethylation of lithium phenylphosphides[132] and the product of the metallation of tetramethylphosphorodiamidous chloride[133] with alkyl halogenomethyl ethers resulted in the formation of the corresponding phosphines and amides of phosphonic acids:

$$Ph_2PLi \rightarrow \begin{cases} \xrightarrow{ClCH_2OMe} Ph_2PCH_2OMe \\ \xrightarrow{ClCH_2OCH_2Cl} Ph_2PCH_2OCH_2PPh_2 \end{cases}$$
$$(Me_2N)_2PCl + Na \rightarrow (Me_2N)_2PNa \xrightarrow{BrCH_2OR[O]} (Me_2N)_2P(O)CH_2OR$$
R = C_1–C_4 alkyl.

(e) Other Methods for the α-Alkoxyalkylation of Tervalent Phosphorus Compounds

α-Alkoxyalkylphosphonates can be sometimes obtained by prolonged heating of trialkyl(aryl) phosphites with aldehydes[134–136]:

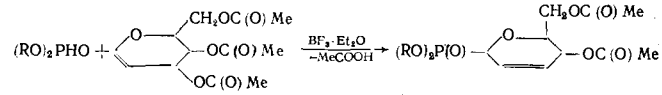
$$(R^1O)_3P + R^3CHO \rightarrow (R^1O)_2P(O)CHR^3OR^1$$
R^1 = Et, Ph; R^3 = H, C_1–C_3 alkyl, $CH_2CH{=}CH_2$, Ph; *p*-MeC_6H_4 .

A chloroform–sodium methoxide mixture alkylates neutral phosphites under mild conditions[137]:

$$R^1O(R^2O)POR^3 + CHCl_3 + MeONa \rightarrow R^1O(R^2O)(R^3O)P(OMe)CH(OMe)_2$$
R^1R^2 = $(CH_2)_2$, R^3 = Me; R^1 = R^2 = R^3 = Me .

Incompletely esterified tervalent phosphorus acids are α-alkoxyalkylated by acetals[138], vinyl ethers[139], keten acetals[140], and the orthoesters of carboxylic[141–144] and carbonic[118] acids:

$$(R^1O)_2PHO + (R^2O)_2CHC_6H_4R^3 \xrightarrow[-R^2OH]{180–210\,^\circ C} (R^1O)_2P(O)CH(OR^2)C_6H_4R^3$$
R^1 = Et, Bu; R^2 = Et; R^2_2 = CH_2CH_2; R^3 = H, OH, NO_2



R = Me, Et

$$(EtO)_2PHO + CH_2{=}C(OEt)_2 \rightarrow (EtO)_2P(O)CMe(OEt)_2$$
$$R^1R^2P(X)H + R^3C(OR^4)_3 \xrightarrow{-R^4OH} R^1R^2P(X)CR^3(OR^4)_2$$
R^1 = OAlk, Et, ClC_3H_1; R^2 = OMe, OEt, Et; R^3 = H, Me, OEt;
R^4 = Me, Et, Pr; X = O, S .

Phosphorylated formals are formed also by the interaction of phosphorous and hypophosphorous acids with an excess of orthoformate[145–149]:

$$H(X)P(O)OH + CH(OR)_3 \rightarrow H(X^1)P(O)OR \xrightarrow[-ROH]{CH(OR)_3} (RO)_2CH(X^1)P(O)OR$$
$X = X^1 = H$; X = OH, X^1 = OR; R = C_1–C_3 alkyl.

Treatment of dialkyl phosphites and diarylphosphine oxides with dimethylformamide methylal leads to phosphinylated aminoacetals[150]:

$$R_2PHO + Me_2NCH(OMe)_2 \rightarrow R_2P(O)CH(NMe_2)OMe + MeOH$$
R = EtO, iso-PrO, Ph.

Phosphonium[23,151,152] and cyclic bisphosphonium salts[132] have been obtained by the alkylation of phosphines with α-chloroalkyl ethers[132]:

$$Ph_3P + ClCHR^1OR^2 \rightarrow Ph_3\overset{+}{P}CHR^1OR^2Cl^-$$
$R^1 = H$; R^2 = Me, Bu; R^1R^2 = $(CH_2)_3$,

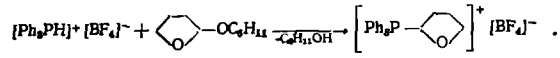
$$Ph_2P(CH_2)_nPPh_2 + ClCH_2OCH_2Cl \rightarrow Ph_2\overset{+}{P}\langle O(CH_2)_n\rangle\overset{+}{P}Ph_2 2Cl^-$$
n = 1, 2 .

The alkylation of triphenylphosphine with 1,2-dibromoethyl ether is accompanied by dehydrobromination[153]:

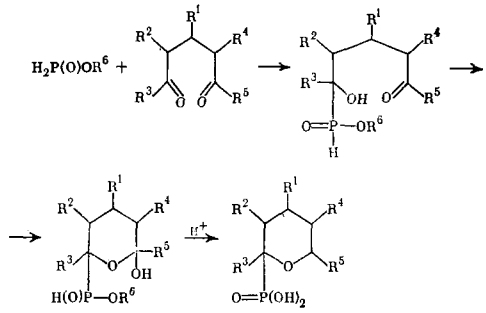
$$Ph_3P + BrCH_2CHBrOEt \xrightarrow{-HBr} Ph_3\overset{+}{P}C(OEt){=}CH_2Br^- .$$

The interaction of triphenylphosphonium tetrafluoroborate and α-cyclohexyloxytetrahydrofuran also leads to an

α-alkoxyalkylphosphonium salt[23]:

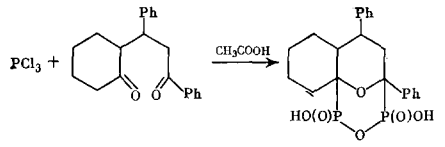


Tetrahydropyranylphosphonates are obtained on heating 1,5-diketones with hypophosphorous acid or alkyl hypophosphites[154–157]:

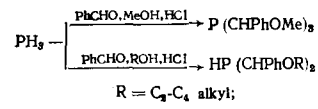


R^{1-5} = H, Ph; $R^2R^3 = (CH_2)_4$; R^6 = H, Et, Bu, CH_2Ph .

The anhydride of tetrahydropyranyldiphosphoric acid has been isolated together with other products in the reaction of 1,5-diketones with phosphorus trichloride in acetic acid[158]:



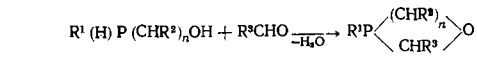
Phosphine[159] and diphenylphosphine[160] react with benzaldehyde and alcohols in the presence of hydrogen chloride to form α-alkoxybenzylphosphines:



R = C_2-C_4 alkyl;

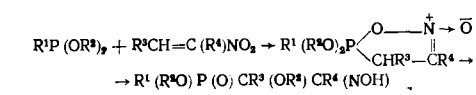
$$Ph_2PH + PhCHO + MeOH \xrightarrow{HCl} Ph_2PCHPhOMe + H_2O \quad .$$

1,3-Oxaphosphorinanes, 1,3-oxaphospholans, and 1,3-oxaphosphepans have been obtained by the reaction of alkyl-ω-hydroxyalkylphosphines with aldehydes[161–166]:



R^1 = Ph, *t-Bu*, C_8H_{17}; R^2 = H, Me, Et, Ph; R^3 = Ph, *t-Bu*; n=2–4

The addition of trialkyl phosphites and dialkyl phosphonites to α,β-unsaturated nitro-compounds with subsequent isomerisation of the intermediate phosphoranes leads to the oximes of α-alkoxy-β-ketophosphonates and phosphinates[167,168]:



R^1 = OR^3, Ph, Me; R^2 = Me, Et; R^3 = Me, Ph, C_6H_4X; R^4 = H, Me .

2. Methods for the Conversion of Substituted Alkyl Groups in Organophosphorus Compounds into α-Alkoxyalkyl Groups

(a) Substitution Reactions of Chloro(sulphonyloxy)methyl Derivatives of Organophosphorus Compounds

This method is of limited importance for the synthesis of compounds with a single α-alkoxyalkyl group at the phosphorus atom, because the methods of synthesis of such compounds described above are more effective. Thus the alkoxylation of arenesulphonyloxymethylphosphonates is accompanied by side reactions involving the transesterification and dealkylation of the ester groups at the phosphorus atom, which lowers the yield and hinders the isolation of the desired products[169]:

$$R^1SO_2OCH_2P(O)(OR^2)_2 + R^3ONa \rightarrow R^3OCH_2P(O)(OR^2)_2 + R^3OCH_2P(O)(ONa)OR^2 + R^3OCH_2P(O)(OR^3)OR^2$$

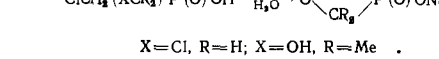
R^1 = Ph, Me; R^2 = iso-Pr, Bu; R^3 = Pr, Bu, C_6H_{13}, $CH_2CHBuEt$, $CH_2P(O)$ (O-Pr-iso)$_2$.

However, this method may be convenient for the synthesis of compounds with two and three α-alkoxyalkyl groups at the phosphorus atom because of the relatively ready availability of, for example, bis- and tris-chloromethyl(hydroxymethyl) derivatives of organophosphorus compounds. Thus bis-alkoxymethylphosphinates[127,170–173] and trisalkoxymethylphosphine oxides[173] have been obtained by this method:

$$(ClCH_2)_nP(O)R^1_{3-n} + nR^2ONa \rightarrow (R^2OCH_2)_nP(O)R^1_{3-n} + nNaCl$$

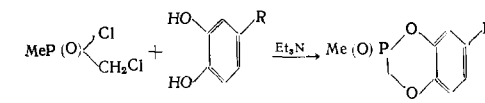
n = 1–3; R^1 = OMe, OEt, OPr, Me, CH_2Cl, Ph; R^2 = C_1–C_8, alkyl, CH_2CH_2OMe, CH_2CH_2OBu .

The interaction of bischloromethyl-[174] and α-hydroxyalkylchloromethyl-phosphinic acids[174,175] with an aqueous solution of sodium hydroxide leads to 1,3-oxaphosphetans:



X = Cl, R = H; X = OH, R = Me .

The reaction of catechol with the chloride of (chloromethyl)-methylphosphinic acid leads to benzo-1,4,2-dioxaphosphorinanes[176]:



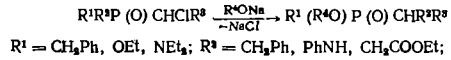
R = H, Me .

The alkylation method has been used to obtain aryloxymethyl derivatives of organophosphorus compounds[171–173,177–181]:

$$(XCH_2)_nP(O)R^1_{3-n} + R^2_mC_6H_{5-m}ONa \xrightarrow{-NaX} (R^2_mC_6H_{5-m}OCH_2)_nP(O)R^1_{3-n}$$

R' = OH, OMe, OEt, OBu, Me; R^2 = Me, Cl, Br, NO_2, COOMe; n = 1 – 3; m = 0 – 3; X = Cl, $OSO_2C_6H_4R^3$; R^3 = Cl, H, Me, NO_2 .

However, in certain cases the reaction of an α-halogenoalkyl derivative of the organophosphorus compound with an alkoxide or phenoxide proceeds differently—with formation of products of nucleophilic[182–184] or pseudoallyl [in the case of phosphorus(III) compounds] rearrangements[185–189]:



R^1 = CH_2Ph, OEt, NEt_2; R^2 = CH_2Ph, PhNH, CH_2COOEt; R^3 = H, Me; R^4 = Me, Ph

$$(ClCH_2)_2P + RONa \xrightarrow{ROH} (ROCH_2)_2P(O)Me + R_2O + NaCl$$

R = C_1 – C_{10} alkyl.

The Darzens reaction constitutes a convenient method of synthesising α,β-epoxyalkyl derivatives of organophosphorus compounds[190–193]:

$$(ClCH_2)_nP(O)(OR^1)_{3-n} + R^2R^3CO \xrightarrow{R^4M} (R^2R^3C{-}CH)_nP(O)(OR^1)_{3-n}$$

R^1 = Me, Et; R^2 = H, Me; R^3 = Et, —CH<, iso-Pent, Ph, p-MeC_6H_4, p-C_6H_4OMe; R^2R^3 = $(CH_2)_6$, o,o'-$C_6H_4C_6H_4$; R^4 = EtO, t-BuO, H; M=Na, K; n = 1,2 .

The reaction of chloromethylphosphonate with dimethyl sulphide, followed by the conversion of the sulphonium salt into an ylid and its subsequent treatment with an aldehyde, is a variant of this reaction[194]:

$$ClCH_2P(O)R^1R^2 + Me_2S \rightarrow [Me_2\overset{+}{S}CH_2P(O)R^1R^2]\,Cl^- \xrightarrow{NaCH_2S(O)Me} \rightarrow [Me_2\overset{+}{S}\overset{-}{C}HP(O)R^1R^2] \xrightarrow{MeCHO} MeCH{-}CHP(O)R^1R^2 + Me_2S$$

R^1 = OEt, OPr, SEt; R^2 = R^1, N(Ph)Me .

(b) Alkylation of α-Hydroxyalkyl Derivatives of Organophosphorus Compounds

The preparative advantages of this method are due to the ready availability of α-hydroxyalkyl derivatives of organophosphorus compounds. Thus treatment of the sodium salts of such compounds[195–205] with alkyl halides yielded a series of alkoxymethyl derivatives of organophosphorus compounds:

$$R^1_nP(O)(CH_2ONa)_{3-n} \xrightarrow[-NaX]{R^3X} R^1_nP(O)(CH_2OR^3)_{3-n}$$

R^1 = alkyl, alkoxy; R^3 = alkyl, CH_2COOEt, $CH_2CH{-}CH_2$, $CH_2CH_2OCH{=}CH_2$, $CH_2SiR^3R^4_2$ (R^3 = Me, Et; R^4 = R^3, OEt); $CH_2C{\equiv}CH$, C(Me)(COOEt)$_2$, C(Me)$_2$C≡CH, C(Me)$_2$C≡C—CH=CH_2; X = Cl, Br; n = 0 – 2 .

Certain hydroxymethyl derivatives of organophosphorus compounds are alkylated directly in the presence of sodium alkoxide or a sodium hydroxide solution[206–210]:

$$(R^1O)_2P(O)CH_2OH + Me_2SO_4 + R^2ONa \rightarrow (R^1O)_2P(O)CH_2OMe + Na_2SO_4 + R^2OH$$

$$(HOCH_2)_nP(O)(OH)_{3-n} + R^1X + R^2ONa \xrightarrow{H^+} (R^1OCH_2)_nP(O)(OH)_{3-n} + NaX + R^2OH$$

R^1 = small alkyl . $CH_2CH{=}CH_2$; R^2 = R^1, H; X = Cl, Br; n = 2,3

The esters and nitriles of acrylic and methacrylic acids also behave as alkylating agents[211]:

$$(R^1O)_2P(O)CHR^4OH + CH^2{=}CR^2R^3 \xrightarrow{R^1ONa} (R^1O)_2P(O)CHR^4OCH_2CHR^2R^3$$

R^1 = Me, Et, iso-Pr; R^3 = HMe; R^3=CN, COOMe; R^4 = H, Me, Et .

The α,β-epoxy-derivatives of organophosphorus compounds are obtained by treating the corresponding halogenohydrins with bases[212–216]:

$$XCHR^1CR^2(OH)P(O)R^3R^4 \xrightarrow{B} R^1CH{-}CR^2P(O)R^3R^4$$

R^1 = H, Me, Ph; R^2 = H; R^1R^2 = $(CH_2)_4$; R^3 = OH, ONH_4, C_1—C_4, alkoxy-group, Ph; R^4 = R^3, $OCHMeCO_2Alk$; B=NaOH, KOH, anion-exchange resin; X = Cl, Br

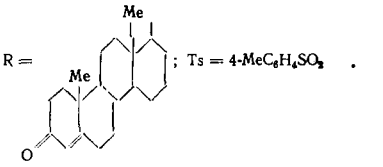
The initial halogenohydrins are usually obtained by the addition of dialkyl phosphites to α-halogenocarbonyl compounds; it is possible to combine the addition and cyclisation stages by adding dialkyl phosphite to the α-halogenocarbonyl compounds in the presence of sodium alkoxide[217–218] or sodium dialkyl phosphite[218–226]:

$$R^1R^3CXC(O)R^3 + (R^4O)_2PONa \rightarrow [R^1R^2CXC(ONa)R^3P(O)(OR^4)_2] \xrightarrow{-NaX} \rightarrow R^1R^3C{-}CR^2P(O)(OR^4)_2$$

R^1 = H, Me; R^2 = R^1, Ph; R^3 = Me, Et, t-Bu, Ph, C_6H_4OMe; R^2R^3 = $(CH_2)_4$; R^4 = Me, Et, Bu, CH_2Ph .

An α-tosyloxyketone has also been used in the latter reaction instead of α-halogenoketones[227]:

$$RC(O)CH_2OTs + (EtO)_2PONa \rightarrow (EtO)_2P(O)CH{-}CHR$$



R = ; Ts = 4-$MeC_6H_4SO_2$.

2-Dialkoxy-2-alkylphosphinyltetrahydrofurans have been obtained by a similar method[223,226]:

$$R^1C(O)CH_2CH_2CH_2Cl + (R^2O)_2PONa \rightarrow (R^2O)_2P(O)C(ONa)R^1CH_2CH_2CH_2Cl \rightarrow \xrightarrow{-NaCl} (R^2O)_2P(O)\text{-}(R^1)\text{-}O$$

R^1 = Me, Et; R^2 = Et, Bu .

When an attempt is made to epoxidise 2-chloro-1-hydroxyethane-1,1-diphosphonic acid with alkali[228,229], the following rearrangement takes place,

$$ClCH_2(HO)C(PO_3H_2)_2 \xrightarrow[2)H^+]{1)NaOH} H_2O_3PCH_2C(O)PO_3H_2 .$$

α,β-Epoxypropylphosphonates have been obtained by treating α-chloroethoxymethylphosphonates (obtained from hydroxymethylphosphonates, acetaldehyde, and hydrogen chloride), with a zinc–copper alloy or phenyl-lithium[230,231]:

$$(RO)_2P(O)CH_2OH + MeCHO \xrightarrow{HCl} (RO)_2P(O)CH_2OCHClMe \xrightarrow{PhLi} \rightarrow (RO)_2P(O)CH{-}CHMe$$

R = Me, Et

The hydroxymethyl groups of bishydroxymethylphosphinic acid are alkylated by epoxyethane[232]:

$$(HOCH_2)_2P(O)OH + CH_2{-}CH_2 \rightarrow (HOCH_2CH_2OCH_2)_2P(O)OCH_2CH_2OH .$$

(c) Other Methods

Epoxyphosphonates are obtained by the epoxidation of the double bond in the α,β-alkenyl derivatives of organophosphorus compounds by biochemical methods[233], peracids[234,235], metal peroxides[236], t-butyl peroxide[237], and hydrogen peroxide in an alkaline medium or in the presence of tungstic

acid salts[235,237–240]:

$$R^1CH{=}CR^2P(O)R^3_2 \xrightarrow{[O]} R^1CH{-}CR^2P(O)R^3_2$$

$R^1 = H$, Me, Ph, OR^4; $R^2 = H$, Me; $R_2 = OH$, ONa, ONH_4, OMe, OEt, OCH_2CH_2Cl, Ph, $C{\equiv}CPh$; $R^4 = Et$, Bu, iso-Bu; $R^1R^2 = (CH_2)_3$, $(CH_2)_4$

$$MeCH{=}CH(R^1O)P(O)OP(O)(OR^1)R^3 + H_2O_2 \xrightarrow{OH^-} MeCH{-}CH(R^1O)P(O)OP(O)(OR^1)R$$

$R^1 = Na$; $R^1_2 = Ca$; $R^3 = OMe$, OEt, OPr, $OCH_2CH_2R^3$, OCH_2COOMe, Me, Ph, CH_2Ph, CH_2COOMe; $R^3 = OMe$, CN, $\overset{+}{N}Me_3$, $CH_2\overset{+}{N}H_2CHMe_2$, $CH_2\overset{+}{N}Me$, CH(Me)OMe.

α-Methyl(phenyl)-β,β-diphenylepoxyethylphosphonates have been synthesised by the reaction of α-ketophosphonates with diphenyldiazomethane[241,242]:

$$(MeO)_2P(O)C(O)R + Ph_2CN_2 \rightarrow (MeO)_2P(O)CR{-}CPh_2$$

$R = Me$, Ph, C_6H_4X, $X = Me$, Cl, Br.

α-Phosphorylated ketals have been obtained by converting α-keto-derivatives of organophosphorus compounds into ketals with the aid of triethyl orthoformate[244]:

$$R^2O(R^1)P(O)C(O)Me + CH(OEt)_3 \xrightarrow{H_2SO_4} R^2O(R^1)P(O)C(OEt)_2Me$$

$R^1 = OBu$, Opent, Ph; $R^2 = Pr$, Bu, Pent.

III. PROPERTIES AND APPLICATIONS

1. Chemical Properties

(a) Substitution Reaction at the Phosphorus Atom

The dichlorides of alkoxymethylphosphonic acids are converted into the dichlorides of alkoxymethylphosphonothioic acids by reaction with phosphorus pentasulphide[58,60,245]. The chlorides of ethylalkoxymethylphosphinic acids and the dichlorides and ester-chlorides of alkoxymethylphosphonic and alkoxymethylphosphonothioic acids readily react with alcohols[7,16,50,58,60,64,110–112], alkoxides[60], and mercaptans[7,60], are converted into fluorides by treatment with arsenic trifluoride[52], are converted into amides by treatment with secondary amines[16,110,112], and are hydrolysed by water to acids[110,112], which are esterified by trialkyl phosphites on heating[146,147,176,208]. The ester-chlorides of alkoxymethylphosphonic acids are readily converted into anhydrides on heating; when the latter react with alcohols or phenols, the monoesters of alkoxymethylphosphonic acids are obtained[68,248]:

$$nR^1O(Cl)P(O)CH_2OR^1 \xrightarrow[-R^1Cl]{\Delta} -[-O-P(O)CH_2OR^1]_n \xrightarrow{nR^2OH} \rightarrow R^2O(HO)P(O)CH_2OR^1$$

$R^1 = C_1$—C_8 alkyl; $R^2 = R^1$, Ph, $C_6H_4NO_2$-*p*.

The diethyl ester of (2-acetoxyethoxy)methylphosphonic acid readily cyclises on heating[249]:

$$MeC(O)OCH_2CH_2OCH_2P(O)(OEt)_2 \xrightarrow{\Delta} \text{(cyclic)}P(O)OEt + MeCOOEt$$

Dibutylethoxymethylphosphine oxide has been obtained by the reaction of diethyl ethoxymethylphosphonate with butyllithium[250].

Like other alkyl esters of phosphonic acids, alkoxymethylphosphonates hydrolyse in an alkaline medium with formation of salts of the monoesters of alkoxymethylphosphonic acids[203], while on refluxing with hydrochloric acid they hydrolyse to alkoxymethylphosphonic acids[4,26,203].

Diethyl diethoxymethylphosphonate is converted, on treatment with hydrobromic acid, into diethoxymethylphosphonic acid, while its treatment with gaseous dry hydrogen chloride is accompanied by the partial dissociation of the C–P bond and leads to a mixture of diethyl phosphite and diethyl ethoxychloromethylphosphonate[90].

The reaction of α-alkoxyalkylphosphonates with an equimolar amount of phosphorus pentachloride yields the ester-chlorides of the corresponding acids in satisfactory yields[19,52].

When an excess of phosphorus pentachloride is used, the C–P bond is cleaved and a complex mixture of products is obtained instead of the expected acid dichloride[251,252]. Analogous processes occur on treatment of α-alkoxyalkylpyrophosphonates and α-alkoxyalkylphosphine oxides with phosphorus pentachloride[252].

When alkylalkoxymethyl derivatives of organophosphorus compounds are acted upon by alkalies under severe conditions, the alkoxymethyl groups are split off[174,189]:

$$(C_8H_{17}OCH_2)_2P(O)Me + KOH \rightarrow C_8H_{17}OCH_2(Me)P(O)OK + C_8H_{17}OMe$$

$$\text{(cyclic)}P(O)R + NaOH \rightarrow MeOCH_2(R)P(O)ONa$$

$R = OH$, Me.

The phenyl groups are split off preferentially in the interaction of quaternary α-alkoxyalkylphenylphosphonium salts with potassium or sodium hydroxide[23,79,152]:

$$Ph_2R^1\overset{+}{P}CHR^2OR^3X^- \xrightarrow{MOH} PhR^1P(O)CHR^2OR^3 + PhH + MX$$

$R^1 = Ph$, Me; $R^2 = H$; $R^3 = Me$; $R^2R^3 = (CH_2)_3$; $X = Cl$, I, BF_4; $M = Na$, K.

α-Alkoxyethyltriphenylphosphonium chloride and α-alkoxy-β-bromoethyltriphenylphosphonium bromide are cleaved by water in a different manner[253–255]:

$$Ph_3\overset{+}{P}CH(OR)MeCl^- \xrightarrow[-HCl]{H_2O} Ph_3P + [MeCH(OH)OR]$$

$$Ph_3\overset{+}{P}CH(OR)CH_2BrBr^- \xrightarrow[-2HBr]{H_2O} Ph_3PO + [ROCH{=}CH_2]$$

$R = Et$, Bu.

When the diethyl esters of α,β-epoxyalkylphosphonic acids are heated with alcoholic solutions of sodium dialkyl phosphites, the diethoxyphosphinyl group is split off and dialkyl esters of β-ketophosphonic acids are formed[256]:

$$(EtO)_2P(O)\text{(cyclic)}CHMe + (R^2O)_2PONa \rightarrow [(EtO)_2P(O)CR^1(ONa)CHMeP(O)(OR^2)_2] \rightarrow$$

$$\rightarrow (EtO)_2PONa + R^1C(O)CHMeP(O)(OR^2)_2$$

$R^1 = H$, Me; $R^2 = Et$, iso-Pr, Bu.

The reduction of alkoxymethyldiphenylphosphine oxides with lithium aluminium hydride or trichlorosilane yielded the corresponding phosphines, which were converted by alkylation into phosphonium salts[79,152]. A cyclic bisphosphonium salt has been synthesised by the alkylation of the bisdiphenylphosphinomethyl ether with ethylene bromide[132]:

$$Ph_2PCH_2OCH_2PPh_2 + BrCH_2CH_2Br \rightarrow Ph_2\overset{+}{P}\text{(cyclic)}\overset{+}{P}Ph_2 \cdot 2Br^-$$

On heating and treatment with acids, zinc chloride, or boron trifluoride etherate, α,β-epoxydiphosphonates[193,212,243,257–259] and 2-methoxy-2-diphenylphosphinyl-1-phenyl-1-propanol[260] are converted into β-keto-derivatives of organophosphorus compounds as a result of α → β migration:

$$(R^1O)_2P(O)\text{(cyclic)}CR^2{-}CR^3R^4 \rightarrow (R^1O)_2P(O)CR^3R^4C(O)R^2$$

$R^1 = Me$, Et; $R^2 = H$, Me, t-Bu, Ph, *p*-XC_6H_4; $X = OMe$, Me, Cl, Br; $R^3 = H$, Ph; $R^4 = H$, Me, Ph; $R^3R^4 = (CH_2)_n$, *o*, *o*′-$C_6H_4C_6H_4$; $n = 3, 5$

$$Ph_2P(O)\underset{\underset{CH(Ph)OH}{|}}{C}(Me)OMe \xrightarrow{CF_3COOH} Ph_2P(O)CH(Ph)C(O)Me$$

(b) Substitution Reaction at the α-Carbon Atom

Treatment of alkoxymethyltriphenylphosphonium chloride with alkyl(aryl)-lithium or alkoxides leads to an ylid, which reacts with aldehydes and ketones to form triphenylphosphine oxide and alkyl vinyl ethers[151,261,262]:

$$Ph_3\overset{+}{P}CH_2OR^1Cl^- \xrightarrow[-B\cdot HCl]{B} Ph_3P{=}CHOR^1 \xrightarrow{R^2R^3CO} R^2R^3C{=}CHOR^1 + Ph_3PO$$

R^1 = Me, Bu, Ph, *p*-MeC_6H_4; $R^2 = R^1$, H; $R^3 = R^1$; $R^2R^3 = (CH_2)_n$; $n = 4-7$.

Alkoxyethylphosphonates are also suitable for the synthesis of the latter[14,16,17,25,26,263]:

$$(R^1O)_2P(O)CH(A)OR^2 \xrightarrow[-RH]{1)MR;2)R^3R^4CO} (R^1O)_2P(O)CA(OR^2)CR^3R^4OM \xrightarrow{\Delta} \rightarrow R^3R^4C{=}C(A)OR^2 + (R^1O)_2P(O)OM \ ;$$

R^1 = Me, Et, Bu; $R^2 = R^1$, Ph, CH_2CH_2OMe; A = P(O)$(OR^1)_2$, COOR^1, $CONH_2$, CONHPr, C(O)Me, CON⟨⟩O, Ph, H; $R^3 = R^1$, H, Ph; $R^4 = R^2$, H, ⟨⟩ , *p*-XC_6H_4; X = OMe, Me, Cl; $R^3R^4 = (CH_2)_n$; $n = 4, 5$, MR = Li, iso-Pr_2NLi, NaH, t-BuOK, n-BuONa.

When α-methoxyethyldiphenylphosphine oxide was allowed to react with lithium di-isopropylamide and then with benzaldehyde, 2-methoxy-2-diphenylphosphinyl-1-phenyl-1-propanol was isolated[260]:

$$Ph_2P(O)CH(Me)OMe \xrightarrow[2)PhCHO;H_2O]{1)\ iso\text{-}Pr_2NLi} Ph_2P(O)C(Me)(OMe)CH(Ph)OH \ .$$

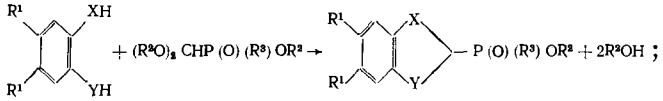
Metallation of alkoxymethylphosphonates followed by treatment with chlorotrimethylsilane, chloromethyl ethyl ether[250], sulphur, and methyl iodide[264] yielded α-substituted phosphonates:

$$(Me_2N)_2P(O)CH_2OEt \xrightarrow[-BuH]{BuLi} (Me_2N)_2P(O)CHLiOEt \xrightarrow[-LiCl]{RCl} (Me_2N)_2P(O)CHROEt \ ;$$

R = $SiMe_3$, CH_2OEt .

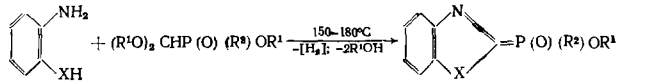
Chlorination of dialkyl methoxymethylphosphonates with sulphuryl chloride leads to α-chloromethyoxymethylphosphonates[9].

Reactions involving the substitution of α-alkoxy-groups are also known. Thus cyclic phosphorylated formals and aminomercaptals are obtained by the transacetalisation of phosphorylated dialkylformals with *o*-bisphenols[265] and *o*-aminothiophenol[266]:



R^1 = H; $R^1_2 = (CH)_4$; R^2 = Et, Pr, Bu; R^3 = OEt, OBu, Ph, *p*-MeC_6H_4; X = Y = O; X = NH, Y = S .

When *o*-aminophenol and *o*-phenylenediamine are used in this reaction, phosphorylated derivatives of benzoxazole and benzimidazole are obtained as a result of the oxidation of the transacetalisation products during isolation[267–268]:



X = NH, O; R^1 = small alkyl; R^3 = Ph, *p*-MeC_6H_4, OR^1 .

α-Dialkylamino-α-methoxymethyl derivatives of organophosphorus compounds interact with thionyl chloride to form phosphorylated ammonium salts[150,269] and also with dialkyl phosphites and diphenylphosphine oxide to form dialkylaminomethanebisorganophosphorus compounds[150]:

$$(EtO)_2P(O)CH(NMe_2)OMe \xrightarrow[R_2PHO]{SOCl_2} \begin{cases} (EtO)_2P(O)CH{=}\overset{+}{N}Me_2Cl^- \\ (EtO)_2P(O)CH(NMe_2)P(O)R_2 \end{cases} ;$$

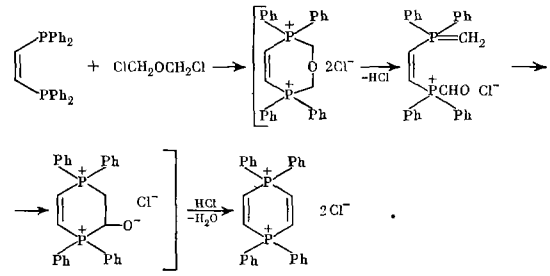
R = OEt, Ph.

α-Alkoxy-β-halogenoethylphosphonates are readily dehydrochlorinated by sodium hydroxide[3], while 2-dialkoxyphosphinyl-3-chloro-1,4-dioxans and α-alkoxy-β-chloroethylphosphine oxides eliminate hydrogen chloride even in the course of distillation[39,40,104,106].

α-Ethoxyvinyltriphenylphosphonium bromide readily combines with thiophenol via its double bond[153]:

$$Ph_3\overset{+}{P}C(OEt){=}CH_2Br^- + PhSH \rightarrow Ph_3\overset{+}{P}CH(OEt)CH_2SPhBr^- \ .$$

The rearrangement occurring in the alkylation of *cis*-bisdiphenylphosphinoethylene with bischloromethyl ether has been described[270]:



2-Diphenylphosphinyl-2-methoxy-1-methyl-3-tosyloxypentane isomerises in an acetate solution as a result of the 2 → 3 migration of the methoxy-group[260]:

$$Ph_2P(O)C(OMe)(CHMe_2)CH(Me)OTs \xrightarrow{AcOH-AcONa} \rightarrow Ph_2P(O)CH(COMe)CHMe_2 + Ph_2P(O)CH(CHMe_2)C(OMe){=}CH_2 \ ;$$

Ts = 4-$MeC_6H_4SO_2$.

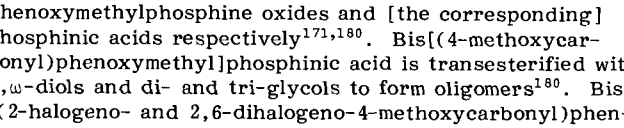
(c) Other Reactions

Propargyloxymethylphosphonates enter into the Mannich reaction[198]:

$$(R^1O)_2P(O)CHR^2OCH_2C{\equiv}CH + CH_2O + HNR^3_2 \xrightarrow{(AcO)_2Cu} \rightarrow (R^1O)_2P(O)CHR^2OCH_2C{\equiv}CCH_2NR^3_2 \ ;$$

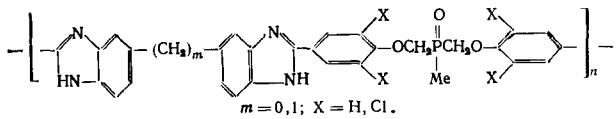
R^1 = Et, Pr, Bu; R^2 = H, Me; R^3=Et; $R^3_2 = (CH_2)_5$.

On treatment with formaldehyde, the disodium salt of phenoxymethylphosphonic acid is hydroxymethylated, while the free acid is converted into a polymer[272]:



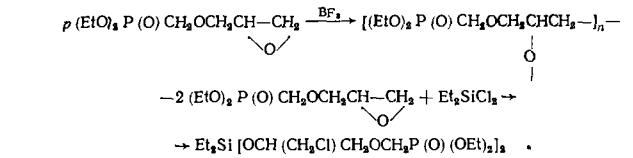
On treatment with sodium hydroxide in alcohol, bis[(4-methoxycarbonyl)phenoxymethyl]phosphine oxides and the corresponding phosphinic acids are converted into carboxyphenoxymethylphosphine oxides and [the corresponding] phosphinic acids respectively[171,180]. Bis[(4-methoxycarbonyl)phenoxymethyl]phosphinic acid is transesterified with 1,ω-diols and di- and tri-glycols to form oligomers[180]. Bis-[(2-halogeno- and 2,6-dihalogeno-4-methoxycarbonyl)phenoxymethyl]methylphosphine oxides and the carboxylic acids obtained from them by hydrolysis respectively undergo transesterification or esterification with ethylene glycol, diethylene glycol, and 1,2-propylene glycol to form thermostable self-extinguishing resins[273–275].

The condensation of bis[(4-methoxycarbonyl)phenoxymethyl]methylphosphine oxide or bis[(4-carboxy-2,6-dichloro)phenoxymethyl]methylphosphine oxide with 3,3'-diaminobenzidine tetrahydrochloride or 3,3',4,4'-tetra-aminodiphenylmethane yields resins with a high thermal stability[276]:



$m = 0,1$; X = H, Cl.

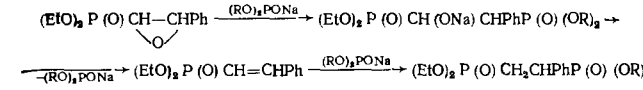
2,3-Epoxypropylenoxymethylphosphonate polymerises on treatment with boron trifluoride[196] and on heating interacts with dichlorodiethylsilane with opening of the oxiran ring[277]:



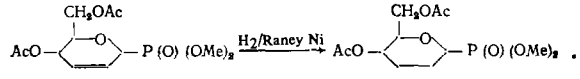
Treatment of epoxyphosphonates with an alcoholic solution of boron trifluoride etherate or sulphuric acid leads to β-alkoxy-α-hydroxyethylphosphonates[237].

The oxiran ring in α,β-epoxyphosphonates is opened to form α-hydroxyphosphonates with β-functional substituents on treatment with an aqueous solution of sulphuric acid, aniline, ammonia[278], water, amines, alcohols, mercaptans, potassium cyanide, and malonates[229,279–283].

Epoxyphosphonates interact with sodium dialkyl phosphite, forming bisphosphonates[284]:



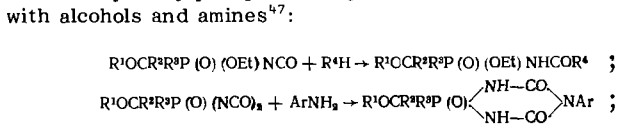
The multiple carbon–carbon bond in unsaturated glycosyl phosphonates is readily hydrogenated under the usual conditions[285]:



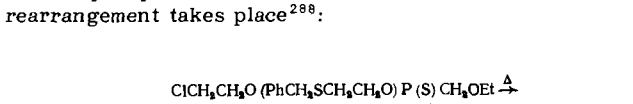
(−)-*cis*-α,β-Epoxypropylphosphonic acid has been isolated from the racemic mixture by resolving the latter with the aid of α-phenylethylamine[286,287].

The β-chloroethyl esters of alkoxymethylphosphonic acids are converted into the β-mercaptoethyl esters on treatment with sodium sulphide and subsequent acidification, while treatment with sodium mercaptide leads to β-alkylthioethyl esters[288]. Alkylation of the silver salt of *cis*-α,β-epoxypropylphosphonic acid with halogeno-derivatives yielded the corresponding esters[289].

α-Alkoxymethylphosphonoisocyanitidates readily combine with alcohols and amines[47]:

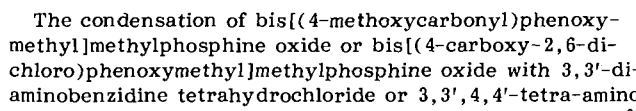


When phosphonothionates are heated, the thione–thiol rearrangement takes place[288]:



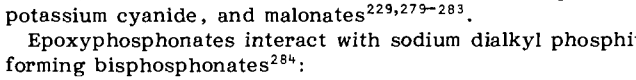
2. Applications of α-Alkoxyalkyl Derivatives of Organophosphorus Compounds

α-Alkoxyalkyl derivatives of organophosphorus compounds have been recommended in several fields. One of these involves their use as pesticides. Certain esters of alkoxymethylphosphono(di)thioic acids have been tested for this purpose. They were found to exhibit a high insectidal activity and a comparatively low toxicity for warm blooded animals[7,56,58,60,104]:



The second application is in medicine: certain compounds of this class, for example mixed alkyl and *p*-nitrophenyl esters of α-methoxyalkylphosphonic acids, have an antienzymatic activity and an insignificant toxicity for mammals and have been recommended for therapy[230]. The esters of bisallyloxymethylphosphinic acid are able to suppress the activity of the central nervous system[210] and are therefore of definite therapeutic interest.

Among α-epoxy-derivatives of organophosphorus compounds, an effective antibiotic has been discovered—1-*R*,2-*S*-1,2-epoxypropylphosphonic acid[191,287,292]; its derivatives, for example, its salts with aminoacids[241], and epoxypropylpyrophosphonic acids also have a high bactericidal activity [240,293]:



The third application involves the use of alkoxymethylphosphine oxides as extractants[294], for example, for uranium and thorium, particularly when the latter are to be extracted from sulphuric acid solutions[189,205]:



The most effective extractants are alkoxymethyldialkylphosphine oxides, whose extracting capacity approaches that of trialkylphosphine oxides[294]. In the above series trisalkoxymethylphosphine oxides are the least effective, but even their activity exceeds by three orders of magnitude that of tributyl phosphate[205].

The fourth practical application involves the use of the products of the polycondensation of bisaryloxymethylphosphinic acids with formaldehyde as ion-exchange resins[177,178,272], which proved to be selective in relation to certain polyvalent ions.

Carboxyalkoxymethylphosphonic acids, for example, $H_2O_3PCH_2OCH_2COOH$, have been recommended as complexones for the prevention of the deposition of salts[202,203].

The fifth application involves the use of di(tri)halogeno-alkoxy(phenoxy)methylphosphonates[6,8,181] and the products resulting from the addition of alcohols, mercaptans, amines, cyanides, sulphides, etc. to α-epoxyphosphonates[278–283] as fire-proofing additives to polymers and textiles.

The possibility of using α-alkoxyalkylphosphonates, α-alkoxyalkylphosphinates, and α-alkoxyalkylphosphine oxides as solvents which effectively solvate alkali metal cations[85,127,188,271,295,296], plasticisers[2,85,170], phytopharmaceutical preparations[8], monomers[177,272], etc. has been indicated. It has also been noted that higher alkoxymethylphosphinic acids have effective surface-active properties[4,297].

After the present review had been sent to the editors, several publications describing the synthesis and properties of α-alkoxyalkyl compounds of phosphorus appeared.

Phosphorus ylids have been obtained by the alkylation of the phosphorus atom in the *C*-phosphorylated malonic ester with alkyl chloromethyl ethers[298] and diethoxymethyl acetate[299].

The interaction of chlorodiphenylphosphine with a series of dimethyl acetals led to the synthesis of α-methoxyalkyldiphenylphosphine oxides[300]. Bis(α-diphenylphosphinyl)benzyl ether has been obtained, together with other products, by heating chlorodiphenylphosphine with benzaldehyde[301].

The alkylation of hypophosphorous acid by orthoformates in the presence of toluene-*p*-sulphonic acid, leading to a mixture of bisdialkoxymethylphosphinate and alkyl dialkoxymethylphosphonite, has been described[302].

The reactions of primary and secondary phosphines with alcohols and aromatic aldehydes in the presence of toluene-*p*-sulphonic acid have been investigated[303]. It has been shown that, depending on the type of substituents in the aromatic ring, either α-alkoxybenzylphosphines or benzylidenebisphosphines are obtained.

A study has been made of the thermal cleavage of 1-alkoxy-2-bromoethyl and α-alkoxyalkyl derivatives of triorganophosphonium salts, involving the formation of triorganophosphine oxide in the former case and triorganophosphine in the latter case[304].

When electrophiles (hydrogen bromide, tetrapropyldiborane) are added to (α-alkoxyvinyl)triphenylphosphonium salts, the directing influence of the alkoxy-group predominates over that of the positively charged phosphorus atom[305].

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Organic Complexes of Univalent Gold

K.I.Grandberg

Studies on the synthesis and reactivities of gold(I) complexes σ-linked to alkyl, aryl, unsaturated, and carbonyl-containing ligands, π-complexes with olefins and acetylenes, anionic, ylid, and carbene complexes, and also gold complexes with a bridging carbon atom derived from an organic group are examined.
The bibliography includes 167 references.

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I. INTRODUCTION

The chemistry of organic complexes of univalent gold has developed extremely vigorously in recent years. The first stable organometallic derivatives of univalent gold of the type RAuL, where L is a ligand containing phosphorus, arsenic, nitrogen, or sulphur, were obtained in 1959; in the first decade research developed mainly on the synthesis of such compounds by traditional methods—using organolithium, organosodium, or organomagnesium compounds. However, in the 1970's there was a qualitative change in the nature of the studies. New types of organic complexes of univalent gold were discovered: π-olefin, π-acetylene, carbene, anionic, and ylid complexes, as well as gold complexes with a bridging carbon atom. Fundamentally new methods of synthesis of organogold compounds were developed and hitherto unknown agents for the introduction of gold were discovered, which made it possible to obtain a wide range of alkyl and aryl complexes of gold(I) with different substituents, including functional groups, in the organic moiety. Furthermore, there has been a growth of interest in the study of the mechanisms of the reactions of organic derivatives of gold, which was aroused primarily by the more extensive utilisation of noble metals and their compounds as catalysts as well as their applications in medicine and radioelectronics.

Several reviews have now been published, most of these dealing with data on the organic complexes of both univalent and tervalent gold[1-5]. Puddephatt's monograph[6], containing extensive information about organic derivatives of gold in different valence states, was published in 1978. However, hitherto there has been no single review on organic complexes of univalent gold.

This review is devoted to the chemistry of such complexes. The data have been arranged systematically in terms of different types of organic complexes of gold(I).

II. σ-COMPLEXES OF THE TYPE RAuL

1. σ-Alkyl and σ-Aryl Complexes of Gold(I)

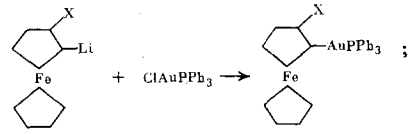
Historically the first and largest class of organic complexes of univalent gold comprises linear σ-alkyl and σ-aryl complexes of the type RAuL. Phosphines are usually employed as the stabilising ligand L;[7] very few examples of complexes with phosphites[8], arsines[9], and isonitriles[10] are known.

(a) Methods of Synthesis

The first phosphine complexes of alkyl- and aryl-gold were obtained in 1959 from complex gold halides and organolithium and organomagnesium compounds. For a long time, this was the only procedure for synthesising compounds of this type[7, 11-13]:

$$PhCH_2MgCl + ClAuPPh_3 \rightarrow PhCH_2AuPPh_3 .$$

Lithium derivatives of aromatic π-complexes (ferrocene and cymantrene) give rise to high yields of organogold σ-complexes on treatment with triphenylphosphine complexes of gold halides[14-16]:



X = H, Cl, OMe, CH_2NMe_2 .

Organogold complexes with ligands such as diphenylferrocenyl- and triphenylferrocenyl-phosphines have been obtained via organolithium and organomagnesium compounds. The diphenylferrocenylphosphine complex of gold bromide reacts with organolithium and organomagnesium compounds like its triphenylphosphine analogue[17]:

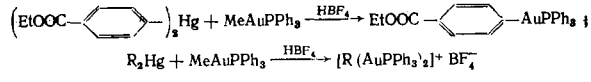
$$BrAuPPh_2C_5H_4FeC_5H_5 \xrightarrow{MeMgI} MeAuPPh_2C_5H_4FeC_5H_5 ;$$
$$BrAuPPh_2C_5H_4FeC_5H_5 \xrightarrow{p\text{-}MeC_6H_4Li} p\text{-}MeC_6H_4AuPPh_2C_5H_4FeC_5H_5 .$$

The triphenylphosphine complex of gold bromide reacts with methylmagnesium iodide, but does not react with aryl- and alkenyl-lithium and organomagnesium compounds[17]:

$$BrAuP(C_5H_4FeC_5H_5)_3 + MeMgI \rightarrow MeAuP(C_5H_4FeC_5H_5)_3 .$$

A preparative method of synthesis of organogold complexes with a wide range of organic groups via organomercury derivatives was proposed in 1978.[18-21] When organomercury compounds R_2Hg are acted upon by a phosphine complex of

methylgold $MeAuPR'_3$ in the presence of HBF_4, either mononuclear or dinuclear organogold complexes are formed depending on the groups R and R' and the reaction conditions[21,22]:



$$R_2Hg + MeAuPPh_3 \xrightarrow{HBF_4} [R(AuPPh_3)_2]^+ BF_4^-$$

where R = ferrocenyl, β-naphthyl, α-thienyl, styryl, cymantrenyl, tolyl, or phenyl.

The dinuclear organogold complexes can be converted into mononuclear complexes readily by treatment with nucleophiles[21,22]:

$$[R(AuPPh_3)_2]^+ BF_4^- \xrightarrow{Cl^-} RAuPPh_3 + ClAuPPh_3 .$$

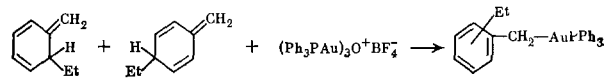
The synthesis of organomonogold complexes from the dinuclear complexes is of significant preparative importance, because a wide variety of dinuclear complexes are obtained in high yields from organomercury derivatives or by inserting gold into ferrocenes (see below).

Perhalogenoaryl derivatives of gold(I) are formed when phosphine complexes of univalent gold salts react with organic derivatives of tervalent thallium[23,24]:

$$(C_6F_5)_2TlBr + MeCOOAuPPh_3 \rightarrow C_6F_5AuPPh_3 + (C_6F_5)TlBr(OCOMe) .$$

Apart from the methods of synthesis of σ-complexes of gold enumerated above, based on the use of various organometallic derivatives or on the gold insertion reaction, single examples of the preparation of complexes of alkyl- and aryl-gold by other methods have been described.

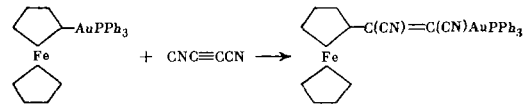
Isomeric trienes, generated from *o*- and *p*-ethyltoluenes, react with tris(triphenylphosphinegold)oxonium tetrafluoroborate via the aromatising metallation mechanism[25] with formation of a benzyl derivative of gold[26]:



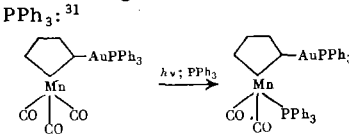
When the triphenylphosphine complex of gold pentafluorobenzoate is heated, it is decarboxylated and pentafluorophenylgold is formed[27,28]:

$$C_6F_5COOAuPPh_3 \xrightarrow{120^\circ} C_6F_5AuPPh_3 + CO_2 .$$

Other organogold compounds have been obtained from the ferrocenyl, cymantrenyl, and methyl derivatives of gold[30-32]. Thus when ferrocenyl(triphenylphosphine)gold is treated with the dinitrile of acetylenedicarboxylic acid, the acid is inserted in the Au–C bond and an organogold derivative of ferrocenyldicyanoethylene is formed[30]:



When cymantrenylgold is treated with triphenylphosphine or is exposed to ultraviolet light, one of the CO groups is substituted by PPh_3:[31]



Fluorinated alkenes react with phosphine complexes of methylgold under ultraviolet irradiation with insertion of the fluoroalkyl group in the Au–C bond[28,29]:

$$CF_2{=}CF_2 + MeAuPPh_3 \xrightarrow{h\nu} MeCF_2{-}CF_2AuPPh_3 .$$

On treatment with CF_3I, the methyl group in the phosphine complex of methylgold is exchanged for the trifluoromethyl group[32]:

$$MeAuPPh_3 + CF_3I \rightarrow CF_3AuPPh_3 + MeI .$$

Diazomethane reacts with the triphenylphosphine complex of gold chloride with insertion of methylene in the gold–chlorine bond and the formation of the chloromethyl derivative of gold[33]:

$$ClAuPPh_3 + CH_2N_2 \rightarrow ClCH_2AuPPh_3 .$$

Aromatic isonitriles react with $ClAuPPh_3$ in alcohol in the presence of alkali to form organic σ-derivatives of gold[34-36]:

$$ClAuPPh_3 + ArNC + ROH \xrightarrow{KOH} Ph_3PAu{-}C(OR){=}NAr .$$

The same complexes have been obtained by the exchange reaction between gold chloride and organosilver compounds[37]:

$$Ph_3PAuCl + Ag{-}C(OEt){=}NC_6H_4CH_3 \rightarrow AgCl + Ph_3PAu{-}C(OEt){=}NC_6H_4CH_3 .$$

The phosphine complexes of arylgold have been isolated after adding phosphine to oligomeric aromatic complexes of the type $(XArAu)_n$.[38]

(b) Properties

The phosphine σ-complexes of organometallic derivatives of univalent gold are solids, which are readily soluble in benzene, chloroform, methylene chloride, and tetrahydrofuran. The complexes are monomeric in solutions, are diamagnetic, and have a linear structure[7,38,39]. The dipole moments of the alkyl and aryl derivatives of the phosphine complexes are lower than those of the corresponding halogeno-complexes: $MeAuPEt_3$ (5.5 D), $MeAuPPh_3$ (5.6 D), $C_6F_5AuPEt_3$ (6.2 D), and $ClAuPEt_3$ (8.4 D); this indicates a low polarity of the Au–C bond[6,7,40,41].

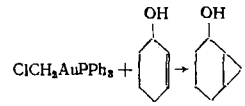
The majority of the phosphine complexes of the type RAuL readily decompose on heating in the solid state and particularly in solutions. The ferrocenylphosphine complexes have the highest thermal stability[17]. The triphenylphosphine complex of methylgold decomposes on heating to 100 °C with formation of ethane, metallic gold, and triphenylphosphine:

$$2MeAuPPh_3 \xrightarrow{100^\circ} C_2H_6 + 2Au + 2PPh_3 ,$$

while heating of ethylgold gives rise to n-butane. It has been shown that the rate of reaction is independent of the presence of oxygen and is retarded after the addition of triphenylphosphine. It has been suggested that the first stage involves the dissociation of the complex with formation of the free phosphine and methylgold, which reacts further with the initial complex[41,42]:

$$MeAuPPh_3 \rightleftarrows MeAu + PPh_3 ;$$
$$MeAu + MeAuPPh_3 \rightarrow C_2H_6 + 2Au + PPh_3 .$$

The triphenylcomplex of chloromethylgold readily decomposes on heating of its benzene solution[33]. If the decomposition is carried out in the presence of 3-cyclohexenol, then the intermediate carbenoid species adds to the double bond with formation of bicyclo[4,1,0]-2-heptanol:



Many organic complexes of gold are sensitive to light. The intermediate formation of methyl radicals has been detected in the photolysis of $MeAuPPh_3$ in deuterochloroform, giving rise

to a set of products: MeD, C_2H_6, $MeCDCl_2$, etc.:[43]

$$MeAuPPh_3 \xrightarrow{h\nu} [MeAuPPh_3]^S \rightarrow [MeAuPPh_3]^T \xrightarrow{CDCl_3} \rightarrow ClAuPPh_3 + Me^{\cdot} + {}^{\cdot}CDCl_2 .$$

The reactivity of organogold complexes is analogous to that of organomercury compounds, but the organogold derivatives are chemically more active and the range of their reactions is much wider. The reactions of complexes of alkyl- and arylgold with a wide variety of reagents, grouped in accordance with several types, are presented below.

A. Reactions with Dissociation of the Au–C Bond

Reactions with protic acids. Protic acids readily cleave the Au–C bond in alkyl and aryl complexes of gold. Thus methyl-,[7] phenyl-,[44] ferrocenyl-,[14] and cymantrenyl-gold[15] react with hydrogen halides, carboxylic acids, and hydrocyanic acid. It has been noted that the triethylphosphine complex of phenylgold is resistant to the action of an aqueous ethanol solution of hydrogen chloride[7]:

$$MeAuPPh_3 + HCl \rightarrow ClAuPPh_3 ,$$
$$PhAuPPh_3 + CH_3COOH \rightarrow CH_3COOAuPPh_3 ,$$
$$C_5H_5FeC_5H_4AuPPh_3 + HCN \rightarrow NCAuPPh_3 .$$

The reaction of aromatic complexes of gold with HBF_4 is specific, giving rise to dinuclear cationic complexes of gold (see below).

The reactions of phosphine complexes of methylgold with benzenethiol[45] and benzeneselenol[46] give rise to methane and gold mercaptide or selenide. The formation of the methyl radical has been detected in the reaction mixture by EPR:

$$MeAuPMe_3 + PhSH \rightarrow PhSAuPMe_3 + CH_4 ,$$
$$MeAuPMe_2Ph + PhSeH \rightarrow PhSeAuPMe_2Ph + CH_4 .$$

On reaction with trifluoromethylacetylene and phenylacetylene, which behave as protic acids, the corresponding gold acetylide is formed[28,29,47]:

$$MeAuPMe_2Ph + CF_3C{\equiv}CH \rightarrow CF_3C{\equiv}CAuPMe_2Ph + CH_4 .$$

Even weak protic acids, such as diphenylphosphine and diphenylarsine, cleave the Au–C bond with liberation of methane and the formation of insoluble gold-containing polymers[46].

Reactions with hydrogen halides and acid anhydrides. The reactions of ferrocenyl- and phenyl-gold with carboxylic acid anhydrides of halides entail the dissociation of the Au–C bond, but products of the electrophilic substitution of the gold atom are not formed[48].

Thus, when ferrocenylgold is treated with acetic anhydride or acetyl chloride, the products are ferrocene, biferrocenyl, a gold(I) salt, and acetaldehyde[48]. On treatment with powerful electrophiles, for example, acetylium and nitronium tetrafluoroborates, ferrocene and biferrocenyl are also obtained and a dinuclear cationic organogold complex is formed: $[R(AuPPh_3)_2]^+BF_4^-$ (see below[48]).

The reactions of phenylgold with carboxylic acid chlorides and nitronium tetrafluoroborate do not give rise to electrophilic substitution products—ketones and nitrobenzene[48]. The results can be readily explained from the standpoint of the mechanism involving one-electron transfer as the first elementary step in the above reactions.

The most convincing example of this is provided by the reaction of ferrocenyl-, phenyl-, or cymantrenyl-gold with ferrocenium tetrafluoroborate, which manifests strikingly the properties of a one-electron acceptor. In the first reaction stage the ferrocenium cation accepts an electron and is converted into ferrocene, while the organogold compound, having lost an electron, decomposes into a radical and triphenylphosphinegold tetrafluoroborate. This coordination-unsaturated compound reacts with a molecule of the initial organogold compound of triphenylphosphine when the latter is added to the reaction mixture[48]:

$$RAuPPh_3 + (C_5H_5)_2Fe^+BF_4^- \rightarrow (C_5H_5)_2Fe + [R^{\cdot}] + [Ph_3PAu^+BF_4^-]$$
$$\downarrow \qquad\qquad \downarrow PPh_3$$
$$R{-}H + R{-}R \quad (Ph_3P)_2Au^+BF_4^- .$$

Reactions with alkyl halides. The experimental data accumulated so far suggest that many reactions of organic complexes of gold(I) involve oxidative addition with subsequent reductive elimination of the resulting gold(III) complex and the formation of new univalent gold complexes†. Only the mechanism of the reactions of phosphine complexes of alkylgold with alkyl halides has been studied in detail[32,49–54].

The interaction of alkylgold complexes with alkyl halides proceeds via oxidative addition, which is characteristic not only of organic derivatives of univalent gold but also of complexes of other transition metals[55]. The final products of the reaction of methyl iodide with the triphenylphosphine complex of methylgold are ethane and the triphenylphosphine complex of gold iodide:

$$MeAuPPh_3 + MeI \rightarrow C_2H_6 + IAuPPh_3 .$$

It has been established experimentally that the reaction proceeds via the following mechanism:

$$MeAuPPh_3 + MeI \rightarrow Me_2AuIPPh_3 ,$$
$$Me_2AuIPPh_3 + MeAuPPh_3 \rightarrow Me_3AuPPh_3 + IAuPPh_3 ,$$
$$Me_3AuPPh_3 \rightarrow C_2H_6 + MeAuPPh_3 .$$

The initial stage of the reaction involves the oxidative addition of methyl iodide to the univalent gold atom. The dimethylgold iodide formed then reacts rapidly with the complex of the initial methylgold, giving rise to a complex of trimethylgold, which undergoes reductive elimination under the reaction conditions with formation of ethane and a gold iodide complex[49–52].

The mechanism proposed has been confirmed by the reactions of other derivatives of alkylgold. Thus the final products of the reaction of triphenylphosphine complexes of ethylgold with methyl iodide are a gold iodide complex and butane[51]:

$$EtAuPPh_3 + MeI \rightarrow (Me)(Et)AuIPPh_3 \rightarrow (Me)(Et)_2AuPPh_3 + IAuPPh_3$$
$$\rightarrow MeAuPPh_3 + C_4H_{10} .$$

When trimethyl- and dimethylphenyl-phosphine complexes of methylgold are used, only the product of the oxidative addition of methyl iodide, namely Me_2AuIL, was isolated from the reaction mixture[53,54]. The complexes of methylgold also react with CF_3I; the nature of the final reaction products depends, as for methyl iodide, on the nature of the ligand[32]. In the case of the trimethylphosphine complex a tervalent gold compound was isolated, while transalkylation takes place in the reaction involving the triphenylphosphine complex. The reaction with the methyldiphenylphosphine ligand gives rise to a mixture of trifluoromethyl derivatives of univalent and tervalent gold[32]:

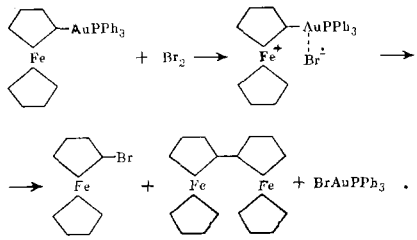
$$MeAuL + CF_3I \rightarrow \begin{cases} \xrightarrow{L=PPh_3} CF_3AuL + MeI \\ \xrightarrow{L=PMe_3} (CF_3)Me_2AuL + IAuL . \end{cases}$$

The triphenylarsine complex of pentachlorophenylgold reacts with MeI to form an oxidative addition product[9].

† The data on this question have been described in detail in Dyadchenko's review (see the next review in this issue).

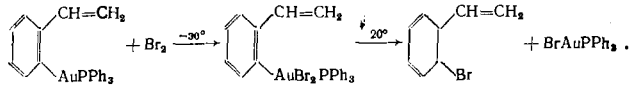
Presumably other reactions, and in particular the reactions of gold(I) complexes with metal halides and salts, proceed analogously, since in some instances the intermediate oxidative addition products have been isolated.

Reactions with halogens. The reactions with bromine and chlorine have been studied in detail in relation to the organogold derivatives of the ferrocene, cymantrene, and benzene series[14,15,44,56,57]. Together with the halogenoderivatives of aromatic systems, compounds of the type RH or R–R are formed in this reaction. For the ferrocenyl compounds of gold, the ratio of bromoferrocene and biferrocenyl varies as a function of the rate and order of mixing of the reactants. When bromine is added rapidly to ferrocenylgold, *mainly bromoferrocene* is formed, while under the conditions of a slow addition there is an appreciable increase of the amount of biferrocenyl. The reaction of ferrocenylgold with bromine and chlorine proceeds specifically also in another respect; at low temperatures in organic solvents an unstable product of the addition of the halogen molecule to the organogold compound is formed initially[56,57]:



It may be that the intermediate complex of ferrocenylgold with a halogen molecule has the structure of a ferrocenium salt, in which the radical-anion is coordinated to the gold atom. This is confirmed indirectly by the finding that in the case of the less reactive organomercury derivatives of ferrocene, a complex of this type has been isolated and investigated[58].

However, one cannot rule out the possibility that the substitution of the $AuPPh_3$ group by bromine or chlorine in the aromatic series involves the oxidative addition of the halogen to the gold atom with subsequent reductive disproportionation of the resulting tervalent gold compound. The possibility of reaction via this mechanism is confirmed by the finding that, in the reaction of *o*-vinylphenylgold with bromine at –30 °C, the product of the addition of the halogen to gold was isolated. At room temperature reductive elimination takes place with formation of gold bromine and *o*-bromostyrene[59]:



Perhalogenoaryl complexes of gold react either with cleavage of the Au–C bond or with its retention and the formation of aryl halide complexes of tervalent gold, depending on the nature of the halogen and the initial complex[9,10,60–64]. Thus the arsine complex of pentafluorophenylgold reacts with chlorine to form only the oxidative addition product; reaction with bromine involves partial cleavage of the Au–C bond in addition to the above reaction, while the reaction with iodine entails the complete cleavage of the Au–C bond[9];

$$C_6F_5AuAsPh_3 + I_2 \rightarrow C_6F_5I + IAuAsPh_3 .$$

The isonitrile complexes of perhalogenoarylgold[62] and the triphenylarsine complex of pentachlorophenylgold react with halogens to form only the oxidative addition products[9].

Reactions with metal salts and organometallic compounds. Organic complexes of gold react with metal salts usually with cleavage of the Au–C bond, but sometimes they proceed with retention of this bond and the formation of the products of the oxidative addition to the gold atom. The reaction of the phosphine complexes of alkyl- and aryl-gold with mercury salts has been studied in greatest detail. Under mild conditions, mercury(II) chloride reacts with methyl-, ethyl-,[65] phenyl-,[44] benzyl-, ferrocenyl-, and cymantrenyl-gold[2], giving rise to high yields of the products of the cleavage of the gold–carbon bond.

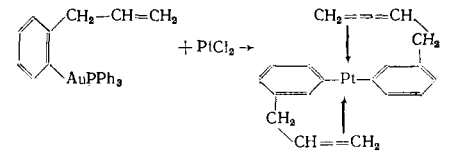
This reaction has served as a model for the investigation of the mechanism of electrophilic substitution at a saturated carbon atom. It has been shown[65] that, for the majority of alkyl complexes of gold, the reaction proceeds via an S_N2 mechanism. Mercury(II) reacts via an S_N1 mechanism in polar solvents with complexes of alkylgold having powerful electron-accepting substituents.

Before the publication of the study of Gregory and Ingold[65], data on the mechanism of substitution in organometallic compounds were obtained mainly in relation to organomercury compounds. However, later a mechanism of the "oxidative addition–reductive elimination" type was proposed as an alternative[49]:

$$RAuPR'_3 + HgX_2 \rightarrow R{-}\underset{\displaystyle X}{\overset{\displaystyle HgX}{\underset{|}{\overset{|}{Au}}}}PR'_3 \rightarrow XAuPR'_3 + RHgX .$$

It is known that adducts corresponding to an intermediate of this type have been obtained for phosphine complexes of iridium[61]. On the basis of the experimental data available at present, it is impossible to make a choice between these two mechanisms.

Both platinum halides[59] and platinum and palladium halide complexes[67] react with complexes of the type of RAuL in which a gold atom is substituted for platinum or palladium:



The complexes of methylgold react with tervalent gold halides and their complexes to form a univalent gold halide and an alkyl derivative of tervalent gold[50,52,54,67]. The reaction involves the transfer of the methyl group from the Au(I) atom to the Au(III) atom[52,68]:

$$2MeAuPMe_2Ph + Br_3AuPMe_2Ph \rightarrow 2BrAuPMe_2Ph + Me_2BrAuPMe_2Ph .$$

In the triphenylphosphine complexes of ethyl- and phenylgold, the Au–C bond is cleaved by $TiCl_3$,[60] while perhalogenoaryl derivatives of gold(I) react with thallium halides via the oxidative addition mechanism with formationof perhalogenoaryl derivatives of gold(III):[9,60,62–64,67]

$$C_6Cl_5AuAsPh_3 + TlCl_3 \rightarrow \textit{cis}\text{-}C_6Cl_5AuCl_2AsPh_3 + TlCl .$$

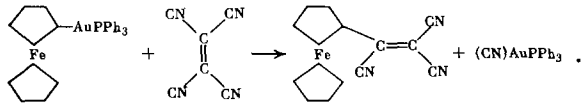
When chloromethylgold is treated with KI and NaCN, chlorine substitution products are not formed. The reaction of chloromethylgold with KI gives a high yield of triphenylphosphinegold iodide, while the reaction with NaCN gives rise to methyltriphenylphosphonium dicyanoaurate[33]. The formation of the latter salt is probably associated with the fact that, when chloromethylgold reacts with NaCN, the CN^- anions are coordinated to the gold atom with ejection of a chloride ion and the stabilisation of the intermediate species as a result of the abstraction of a proton from the solvent

with subsequent migration of the methyl cation, leading to the formation of a phosphonium salt:

$$ClCH_2AuPPh_3 \xrightarrow{2CN^-} \left[Ph_3PAu(CN)-CH_2-CN \right]^- \xrightarrow{H_2O} [Ph_3PCH_3]^+[Au(CN)_2]^- .$$

The triphenylphosphine complex of phenylgold exchanges the phenyl group for the perfluorophenyl group on treatment with $(C_6F_5)_2TlAr$.[24]

Other reactions. The reactions of phosphine complexes of ferrocenyl- and phenyl-gold with tetracyanoethylene (TCE) at room temperature proceed in different ways. In the reaction of ferrocenylgold one of the CN groups is substituted by the ferrocenyl residue, while in the reaction of phenylgold two $AuPPh_3$ groups add to the double bond of TCE:[2,29]



The phosphine complexes of methylgold react with hexafluoroacetone to form a product of addition of the carbonyl group, containing two $AuPPh_3$ groups[27,28]:

$$MeAuPPH_3 + (CF_3)_2C{=}O \rightarrow C_2H_6 + Ph_3PAu{-}O{-}C(CF_3)_2{-}AuPPh_3 .$$

The reaction with hexafluoroacetone hydrate gives rise to $(CF_3)_2C(OAuPPh_3)_2$.[28]

B. Reactions with Retention of the Au–C Bond

The reactions of RAuL with retention of the gold–carbon bond but with a change in the oxidation state of gold take place when the complexes interact with alkyl halides, halogens, and metal salts (see above). The reactions involving the substitution of the ligand L by another less strongly bound ligand without the dissociation of the Au–C bond have been described for complexes of the type RAuL. In the arylgold compounds the Ph_3P ligand has been replaced by the more electron-donating triferrocenylphosphine ligand[17]:

$$p\text{-}CH_3C_6H_4AuPPh_3 \xrightarrow{P(C_5H_4FeC_5H_5)_3} p\text{-}CH_3C_6H_4AuP(C_5H_4FeC_5H_5)_3 .$$

Alkylphosphines are readily displaced from the complex by triphenylphosphine[68]:

$$MeAuPMe_3 + PPh_3 \rightarrow MeAuPPh_3 + PMe_3 .$$

On the basis of such exchange reactions, the series based on the electron-donating properties of the ligands in the methylgold complexes has been established[68]:

$$PPh_3 > PEt_3 > PMe_3 \geqslant AsPh_3 .$$

It has been shown that the exchange of ligands in methylgold complexes involves an associative mechanism[8,69,70]:

$$MeAuL \underset{-L'}{\overset{+L'}{\rightleftharpoons}} MeAu\begin{matrix} L' \\ L \end{matrix} \rightleftarrows MeAuL' .$$

The exchange of a monodentate ligand for a bidentate ligand has been achieved in methylgold complexes[68]:

$$MeAuPMe_3 + Me_2P{-}CH_2{-}CH_2PMe_2 \xrightarrow[-PMe_3]{} \underset{AuMe}{MeP}{-}CH_2{-}CH_2{-}\underset{AuMe}{PMe_2} .$$

In the σ-linked complexes $Ph_3PAu{-}C(OR){=}NAr$ there is a nitrogen atom capable of complex formation. Complexes of this type readily give rise to picrates and also behave as unusual organometallic ligands in relation to another transition metal[71]:

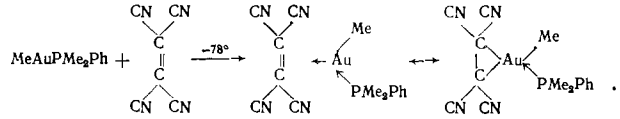
$$Ph_3PAu{-}C(OMe){=}NC_6H_4Me + Rh_2(CO)_4Cl_2 \rightarrow Ph_3PAu{-}C(OMe){=}NC_6H_4Me$$
$$\downarrow$$
$$Cl{-}Rh(CO){-}CO$$
$$\downarrow$$
$$CO$$

C. Reactions Involving Insertion in the Au–C Bond

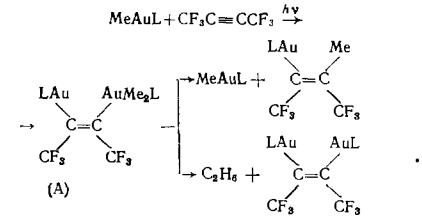
Methylgold complexes react with fluorinated alkenes under ultraviolet irradiation with insertion of the fluoroalkyl fragment in the Au–C bond[27–29]. It may be that the reaction proceeds via the intermediate formation of a π-complex with the olefin:

$$MeAuPPh_3 + CF_2{=}CF_2 \xrightarrow{h\nu} MeCF_2{-}CF_2AuPPh_3 .$$

The phosphine complexes of methylgold react with TCE at low temperatures to form a very unstable 1 : 1 complex[29,47]. The parameters of the infrared and ultraviolet spectra of this complex are inconsistent with the usual charge-transfer complexes of the product involving the insertion of the TCE fragment in the Au–C bond. On the basis of these spectroscopic data and by analogy with the isoelectronic phosphine complex of platinum[72], a metal-containing ring structure was attributed to the tetracyanoethylene complex of methylgold:



The reactions with alkynes sometimes lead only to the product of the insertion of the alkyne in the carbon–metal bond; in most instances a mixture of products is formed[28]. In the reaction of phosphine complexes of methylgold with hexafluorobut-2-yne under ultraviolet irradiation or on heating, a product (A), incorporating a *cis*-bridged C_4F_6 fragment and two gold atoms in different oxidation states, is formed initially[27,47,73,74]. ^1H NMR, Mössbauer spectroscopic, and X-ray spectroscopic data, confirming the proposed structure, are available for this product with L = PMe_3:[47,73,75]



In the presence of an excess of hexafluorobut-2-yne the intermediate (A) can decompose in a manner which depends on the nature of the ligand and the solvent: either with elimination of MeAuL and the formation of the product of the insertion of the $CF_3C{=}CCF_3$ group in the Au–C bond or with reductive elimination at the Au(III) centre and formation of ethane and $(AuL)CF_3C{=}CCF_3(AuL)$. In both cases the *cis*-derivatives of hexafluorobut-2-ene are formed.

In the reaction of but-2-yne with methylgold, only $Ph_3PAuMeC{=}CMeAuPPh_3$ was isolated in a low yield[28] while the reaction with $MeOOCC{\equiv}CCOOMe$ involves decomposition to metallic gold and the formation of two products, one of which results from the insertion of acetylene in the Au–C bond, while the other is *cis*-$LAuMe_2(MeOOC)C{=}C(COOMe)Me$.[29] Ferrocenylgold reacts with acetylenedicarboxylic acid to form the product of the insertion of the alkyne in the Au–C bond (see above).

Methylgold[29] and arylgold[59,76,77] react with SO_2 at low temperatures, SO_2 being inserted in the Au–C bond with formation of gold sulphinate complexes:

$$RAuPPh_3 + SO_2 \rightarrow R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-AuPPh_3 ;$$

$$R = Me,\ o\text{-}CH_2{=}CHC_6H_4 .$$

It has been shown that, in contrast to copper and silver sulphinate complexes in which the metal atom is linked to the oxygen atom, the gold sulphinate complexes have the Au–S bond[29,59,76,77].

2. σ-Alkenyl Complexes of Gold(I)

The σ-alkenyl complexes have been obtained by the reaction of complex gold halides with organosodium[79] or organomagnesium[13,79,80] compounds:

$$C_5H_5Na + ClAuPPh_3 \rightarrow C_5H_5AuPPh_3 ;$$
$$CH_2{=}CHMgBr + ClAuPPh_3 \rightarrow CH_2{=}CHAuPPh_3 .$$

The synthesis via organomercury derivatives is more general[22,81]. Depending on the nature of the alkenyl group and the ligand, the reaction of organomercury compounds with the methylgold complex in the presence of HBF_4 gives rise to either mononuclear organogold complexes:

$$[PhCH{=}C(COOMe)]_2Hg \xrightarrow{MeAuPPh_3;HBF_4} PhCH{=}C(COOMe)AuPPh_3$$

or to the dinuclear complexes, which can be readily converted into the mononuclear complexes by treatment with various nucleophiles:

$$(PhCH{=}CH)_2Hg \xrightarrow{MeAuPPh_3;HBF_4} [PhCH{=}CH(AuPPh_3)_2]^+BF_4^- .$$

The σ-alkenyl complexes are also formed when methylgold interacts with acetylenic compounds via the insertion of the unsaturated group in the Au–C bond (see above).

The σ-alkenyl complexes of gold are solids stable in air, which are readily soluble in chloroform, methylene chloride, and benzene; they are associated in solution in benzene. The styryl derivatives of gold are coloured yellow.

The cyclopentadienyl derivatives of gold may be expected to have either the η^5-structure, similar to that of the triphenylphosphine complex of cyclopentadienylcopper[82], or the η^1-structure, established for the cyclopentadienyl derivatives of mercury. Careful analysis of infrared and ^1H NMR spectra of the triethyl- and triphenyl-phosphine complexes of cyclopentadienyl- and methylcyclopentadienyl-gold, obtained at different temperatures, showed that, like the cyclopentadienyl derivatives of mercury, these compounds constitute an example of stereochemically non-rigid organometallic compounds with η^1-coordination of the cyclopentadienyl ligand[78,84,85].

The reactivity of the alkenyl derivatives of gold has been studied mainly in relation to vinylgold. The gold–carbon bond is readily broken by hydrogen halides, halogens, dithiocyanogen, and mercury salts. The vinyl derivative of gold is resistant to the reaction of dilute acetic and hydrochloric acids:

$$\begin{array}{ccc} PhCOOAuPPh_3 & & ClAuPPh_3 \\ \uparrow PhCOOH & & \uparrow HCl \\ NCSAuPPh_3 \xleftarrow{(SCN)_2} & CH_2{=}CHAuPPh_3 & \xrightarrow{Hal_2} HalAuPPh_3 \\ \downarrow HgCl_2 & & \downarrow KMnO_4;\ Me_2CO \\ CH_2{=}CHHgCl + ClAuPPh_3 & & MeC(O)CH_2AuPPh_3 \end{array} ;$$

$$Hal = Cl,\ Br,\ I .$$

When an acetone solution of $KMnO_4$ was allowed to react with vinylgold, a stable product of the oxidation of the vinyl group was not isolated, gold-substituted acetone being obtained[86].

Reactions involving the cleavage of the gold–carbon bond have been used to confirm the configuration of the styryl derivatives of gold. Thus the interaction of *trans*-styrylgold with iodine in dimethylformamide (DMF) or with mercury(II) bromide yielded the *trans*-isomers of the corresponding styrene derivatives[80]:

$$trans\text{-}PhCH{=}CHAuPPh_3 \begin{cases} \xrightarrow[DMF]{I_2;CdI_2} trans\text{-}PhCH{=}CHI + IAuPPh_3 \\ \xrightarrow{HgBr_2} trans\text{-}PhCH{=}CHHgBr + BrAuPPh_3 . \end{cases}$$

trans-Styryl(triphenylphosphine)gold is unusually readily converted into the *cis*-isomer. Whereas for the mercury derivatives this transition requires a high temperature, ultraviolet irradiation, or treatment with peroxides, the transformation of *trans*-styrylgold into the *cis*-isomer takes place when its solutions are allowed to stand at room temperature or in chromatography on Al_2O_3.[80]

In order to determine the configuration of the phosphine complexes of 1-methoxycarbonyl-2-phenylvinylgold, they were protolysed[22] and *trans*-cinnamic acid and the corresponding gold chloride complexes were isolated in high yields.

3. σ-Alkynyl Complexes of Gold(I)

Gold acetylide C_2Au_2 was obtained as early as 1900; it is an explosive powder with a polymeric structure[87]. Other alkynyl complexes, for example, gold phenylacetylide, proved to be more stable. These complexes have been obtained by treating gold halides with alkali metal acetylides[88]. Gold phenylacetylide was isolated after gold ketenide had been treated with phenylacetylene[89].

A series of very stable gold phenylacetylide complexes with phosphines, arsines, amines, and isonitriles were obtained in 1962. They are formed readily from sodium phenylacetylide and gold halides in the presence of the corresponding ligand[40]:

$$PhC{\equiv}CH \xrightarrow{1)CH_3COONa;\ 2)AuBr} (PhC{\equiv}CAu)_n \xrightarrow{L} PhC{\equiv}CAuL .$$

Yet another method of synthesis of these compounds involves the reaction of an alkyne with methylgold complexes[28,29,47]:

$$MeAuL + RC{\equiv}CH \rightarrow RC{\equiv}CAuL + CH_4 ;$$
$$R = Ph,\ CF_3 .$$

Gold phenylacetylides, stabilised by n-donor ligands, are thermally stable solids, which are readily soluble in many organic solvents; they are usually monomeric in solution with exception of the amine complexes[6,40]. The amine complexes are associated via hydrogen bonds[90]. The activity of the σ-alkynyl complexes has not been studied. It is only known that gold phenylacetylide gives rise to diphenylbutadiyne in the presence of $CuCl_2$:[91]

$$2PhC{\equiv}CAu + CuCl_2 \rightarrow PhC{\equiv}C{-}C{\equiv}CPh + CuCl + 2AuCl .$$

4. Carbonyl-Containing Derivatives of Gold(I)

α-Gold-substituted ketones, gold-substituted acetaldehyde, β-dicarbonyl-gold containing complexes, and gold ketenide are now known. Gold-substituted carbonyl compounds of various types have become readily available after the discovery of a new gold-substituting agent—tris(triphenylphosphinegold)oxonium salts[92,93].

Gold-containing oxonium salts are obtained in high yields in the reaction of coordination-unsaturated cation Ph_3PAu^+ with water in an alkaline or acid medium. The Ph_3PAu^+ ion is generated in solution when triphenylphosphinegold chloride reacts with silver tetrafluoroborate[5].

The most convenient method of synthesis of tris(triphenylphosphinegold)oxonium salts is the reaction of triphenylphosphinegold halides with silver oxide and sodium tetrafluoroborate or potassium permanganate[93]:

$$Ph_3PAuX + Ag_2O \xrightarrow{NaBF_4} (Ph_3PAu)_3O^+BF_4^- \quad (Ph_3PAu)_3O^+MnO_4^- \ (KMnO_4);$$
$$X = Cl, Br.$$

X-Ray diffraction study of tris(triphenylphosphinegold)-oxonium tetrafluoroborate showed that the $(Ph_3PAu)_3O$ fragment has a pyramidal structure: the oxygen atom is displaced from the plane formed by the three gold atoms. The Au–Au distances are 3.03 and 3.215 Å, which suggests Au–Au interaction in the oxonium cation[5].

Gold-containing oxonium salts are crystalline substances, which melt with decomposition and are decomposed by halide ions. Thus treatment of a solution of a tris(triphenylphosphinegold)oxonium salt in chloroform with an aqueous NaCl solution results in a quantitative yield of triphenylphosphinegold chloride and sodium hydroxide[93]:

$$(Ph_3PAu)_3O^+BF_4^- + 3NaCl + H_2O \rightarrow 3Ph_3PAuCl + NaBF_4 + 2NaOH.$$

Gold-containing oxonium salts proved to be excellent gold-substituting agents—this is the first example of the utilisation of metal-containing oxonium salts as metallating agents. Gold-containing oxonium permanganate reacts with acetone and other ketones containing the methyl group, forming ketones substituted with gold in the methyl group[94]:

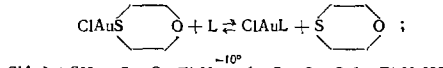
$$R{-}C(O){-}CH_3 + (Ph_3PAu)_3O^+MnO_4^- \rightarrow R{-}C(O){-}CH_2AuPPh_3;$$
$$R = Me, Et, Ph, C_5H_5FeC_5H_4.$$

Gold-substituted acetone and acetylacetone have also been obtained by the reaction of triphenylphosphinegold bromide, silver oxide, and the corresponding ketone[95]:

$$Ph_3PAuX + Ag_2O \xrightarrow[Me_2CO]{X=Br} MeC(O)CH_2AuPPh_3 \quad \xrightarrow[(MeCO)_2CH_2]{X=Cl} (MeCO)_2CHAuPPh_3.$$

The cation Ph_3PAu^+, the structural unit of many gold compounds, is a soft Lewis acid and does not usually form bonds with hard oxygen-containing anions. Thus the gold atom in gold acetylacetonate is linked to a carbon atom, while the atoms of the majority of transition metals, including copper and silver, are linked to an oxygen atom in diketonates[96]. The gold–carbon bond is also formed in gold-substituted ketones and in gold-substituted acetaldehydes[94,97]. α-Gold-substituted carbonyl compounds have also been obtained by the reaction of a gold-containing oxonium salt with enol ethers[5]. When vinyl ethers and esters are treated with oxonium tetrafluoroborate, gold-substituted acetaldehyde is formed[94,97].

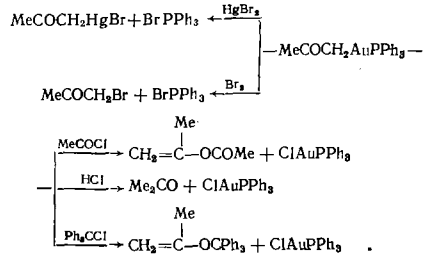
Like copper and silver, gold forms the ketenide $Au_2C{=}C{=}O$ when a gold chloride complex is treated with keten at −10 °C in acetonitrile in the presence of 2,6-dimethylpyridine (L) and triethylamine[89]:



$$ClAuL + CH_2{=}C{=}O + Et_3N \xrightarrow{-10^\circ} Au_2C{=}C{=}O{\cdot}L + Et_3N{\cdot}HCl + L.$$

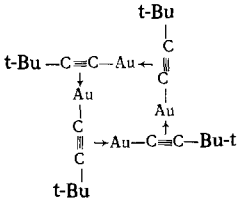
The complex gold ketenide readily loses the ligand at room temperature and gives rise to a polymeric gold ketenide, which is explosive in the solid state and is virtually insoluble in the majority of organic solvents. In the presence of aniline, gold ketinide reacts with phenylacetylene to form acetanilide and gold phenylacetylide.

The reactions of α-gold-substituted carbonyl compounds have been studied in greater detail in relation to gold-substituted acetone. Thus triethylenephosphinegold-substituted acetone reacts with electrophiles similarly to the reaction of α-mercurated carbonyl compounds, with cleavage of the metal–carbon bond and the formation of the corresponding *C*- and *O*-derivatives. The reactions involving the carbon atom proceed with acids, mercury(II) chloride, diazomethane, and bromine[5,33,98]. The reactions involving the O atom take place with carboxylic acid chlorides and chlorotriphenylmethane:



5. The Complexes $(RAu)_n$

There are few example of organic gold complexes of the type $(RAu)_n$ which exist without an outer stabilising ligand L. In such complexes the group σ-linked to the gold atom usually contains either a multiple bond or a heteroatom, which play the role of complex-forming agents in relation to another gold atom, giving rise to oligomerisation or polymerisation of the compound. Examples of such compounds are the σ-alkenyl and σ-alkynyl derivatives of gold. It has been suggested that gold t-butylacetylide exists in the form of a tetramer, for which the following structure has been proposed[1]:



The study of the infrared spectra of this and other alkynyl complexes of gold has shown that the π-coordination of the gold atom with a triple bond is extremely weak[40,88]. In oligomers this bond is readily ruptured even after the addition of a ligand having very weak electron-donating properties, for example Et_3As.[6]

An example of a compound in which intermolecular coordination involves the double bond is provided by cyclopentadienylgold, obtained when an olefin complex of gold chloride is treated with cyclopentadienylsodium or cyclopentadiene in the presence of triethylamine[78]:

$$C_5H_5Na + ClAuL \rightarrow (C_5H_5Au)_n + L + NaCl.$$

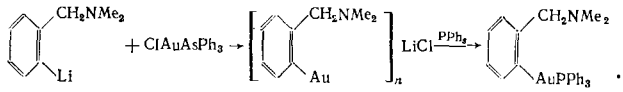
Cyclopentadienylgold is a yellow powder stable only up to −30 °C and almost insoluble in organic solvents. It has a polymeric structure. On treatment with PPh_3, its triphenylphosphine complex is readily produced[78].

Another group of complexes of the type $(RAu)_n$ includes compounds in which the σ-linked ligand contains a nitrogen atom, which functions as a complex-forming agent.

The only phenyl derivatives of gold which exists without a stabilising outer ligand, is 2-dimethylaminomethylphenyl gold[38], obtained from the mixed Au–Li cluster of arylgold:

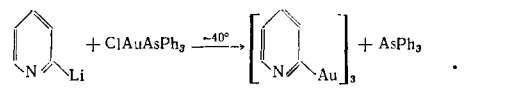
$$R_4Au_2Li_2 + Me_3SnBr \rightarrow RSnMe_3 + (RAu)_n + LiBr\ ;$$
$$R = 2\text{-}Me_2NCH_2C_6H_4\ .$$

The same compound is also formed in the reaction of the lithio-derivative of dimethylaminomethylbenzene with the triphenylarsine complex of gold chloride. Triphenylarsine was isolated in a quantitative yield and a solid residue, consisting of an LiCl–RAu mixture, was obtained, but the pure derivative of arylgold could not be isolated from this mixture. The formation of the latter was confirmed by the isolation of its stable triphenylphosphine complex after the addition of PPh_3 to the reaction mixture[38]:

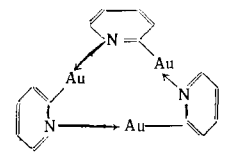


2-Dimethylaminomethylphenylgold is a colourless substance, thermally stable up to 117 °C, has a polymeric structure, and is almost insoluble in organic solvents. The group (containing a nitrogen atom) σ-linked to the gold atom plays the role of the stabilising ligand for the gold atom in another molecule.

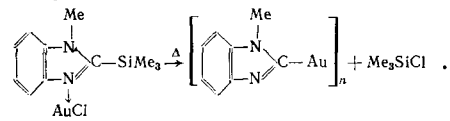
A coordination of the same type can be proposed for pyridylgold and other nitrogen-containing aromatic heterocycles. Derivatives of pyridyl- and quinolinyl-gold have been obtained via their lithio-derivatives and triphenylarsine complexes of gold chloride[99,100]:



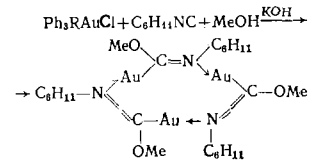
These compounds are solid, sparingly soluble polymeric substances, stable in air at room temperature, which are sensitive to the action of light. The structure of a cyclic trimer with coordination of the nitrogen atoms to the gold atoms has been proposed for pyridylgold:



Yet another example of complexes of this type is provided by the gold-containing derivatives of 1-methylbenzimidazole[101]:



The reaction of aliphatic isonitriles with gold chloride complexes in the presence of alcohol and alkali results in the formation of alkoxy(alkylamino)methylgold complexes[34–36], which are trimeric in solution and, like pyridylgold, have a planar heteroatomic ring:



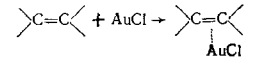
Similar cyclic trimers have been obtained from carbene complexes of gold[102] (see also Section V below).

Cyclic trimers are stable solids, do not react with CO and PPh_3 under normal conditions[36], and react with bromine and iodine via the oxidative addition mechanism, forming cyclic trimeric complexes of tervalent gold[103].

III. π-OLEFIN AND π-ACETYLENE COMPLEXES OF GOLD

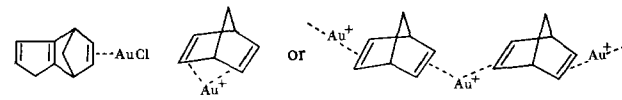
The first olefinic π-complexes of gold(I) were described by Hüttel and Dietyl[104] and Chalk[105]. Complexes of this type are intermediates in reactions involving an olefin and gold compounds as catalysts[106].

The π-complexes of gold(I) are formed at low temperatures as a result of the interaction of the olefin with gold chloride[107,108]:



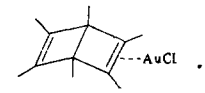
Both acyclic and cyclic olefins undergo the reaction[107–109]. The π-complexes of gold(I) are relatively unstable and readily split off the olefin ligand. Their stability increases with increase of the molecular weight of the olefin[107]. A stable complex has only been isolated for $C_{12}H_{24}$ and olefins with higher molecular weights[107]. Stable π-complexes of cyclic olefins have been isolated only for cycloheptane and compounds with larger rings[109]. The complexes with dienes and trienes are more stable than the corresponding complexes of mono-olefins[107,109,110].

The structure of the complexes cannot be regarded as reliably established, since there are no X-ray diffraction data and a conclusion has been reached about the structure of the complexes on the basis of infrared spectroscopic and ^1H NMR data. A structure in which gold is coordinated to one of the two double bonds has been proposed for the dicyclopentadienyl π-complex; in norbornadiene both double bonds participate in the formation of the π-complex[109]:

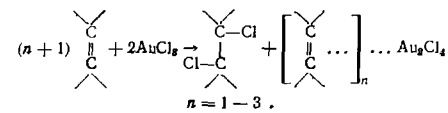


Cyclo-octatetraene reacts with AuCl at −45 °C to form an unstable complex of unknown structure, which is almost fully dissociated in ethereal solution[111].

Hexamethyl-substituted Dewar benzene reacts with AuCl to form a π-complex with coordination of the gold atom to only one of the double bonds of the diene[112]:

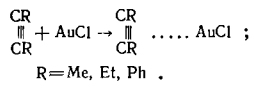


After the interaction of olefins with tervalent gold salts at low temperatures, complexes were isolated with an overall formula corresponding to the composition Au_2Cl_4.olefin.[105,108,111,113] However, the diamagnetism of these compounds as well as Mössbauer spectroscopic data show that one is dealing not with bivalent gold compounds but with a mixture of gold(I) and gold(III) derivatives formed on reduction of half of the initial gold(III) salt by the excess olefin[114]:



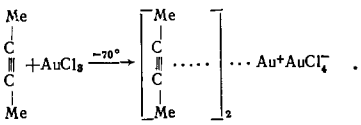
With cyclo-octatetraene (COT), a complex of the same type, having the composition $COT.Au_2Cl_4$, was obtained[111].

Hüttel and Forkl[115] were the first to isolate π-complexes of gold salts with alkynes. The interaction of substituted acetylenes with AuCl at low temperatures leads to the formation of relatively unstable complexes (with the exception of the toluene complex):

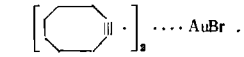


R=Me, Et, Ph .

Pyridine readily displaces the unsaturated ligand from these complexes, giving rise to AuCl.Py (Py = pyridine). If the same alkynes are acted upon by anhydrous $AuCl_3$ at temperatures between −30° and −70 °C, complexes having the composition $(alkyne)_2.Au_2Cl_4$ are formed. They are mixed complexes of univalent and tervalent gold, similar to those described previously for olefinic π-complexes[115,116]:



A π-complex of gold with a cyclic alkyne has been obtained recently. Cyclo-octyne reacts with AuBr to form a stable 2 : 1 π-complex: [117]



The fact that the complex has the cyclo-octyne and not the diene structure has been confirmed by its reaction with cyclone as well as infrared spectroscopic data. The diene synthesis reaction led to the isolation of the corresponding adduct[117].

IV. ANIONIC COMPLEXES OF GOLD

In the first studies on the synthesis of alkyl derivatives of gold using alkyl-lithium compounds, it was already postulated that anionic complexes of the type $(R_2Au)^-$ may be formed[40]. A detailed investigation of anionic gold complexes was begun with the studies of Tamaki and Kochi[118]. After the addition to an ethereal solution of MeAuL of an equivalent amount of methyl-lithium at a low temperature, the authors[118] were the first to detect by ^1H NMR the formation of an anionic complex of dimethylgold[118,119]:

$$MeAuL+MeLi\rightarrow[Me_2AuL]^-Li^+ .$$

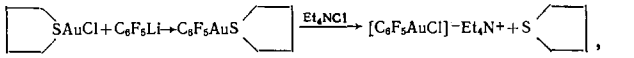
Asymmetric anionic complexes with different alkyl radicals, for example, $[(Me_3C)MeAuL]^-Li^+$, are formed also under the same conditions[118].

The attempts to isolate dialkylaurates with phosphine ligands were unsuccessful. However, it was possible to isolate and characterise a pyridine complex of the lithium salt of dimethylgold, which is unstable in air[118]:

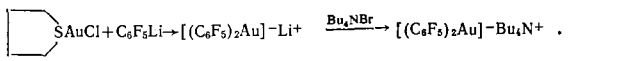
$$[Me_2AuL]^-Li^+ + Py \rightarrow [Me_2AuPy_2]^-Li^+ .$$

When the aprotic polyamine *N,N,N',N''*,*N''*-pentamethyldiethylenetriamine (PMDT) was used as the chelating agent for the lithium ion in the reaction of methylgold with methyl-lithium, a white solid, having the composition $Li(PMDT)AuMe_2$, was isolated. It is stable in the solid state in the light and at room temperature for several months, but rapidly decomposes in protic solvents and under the influence of atmospheric moisture[120]. Spectroscopic study of this hitherto unique stable representative of dialkylanionic complexes showed that it is made up of a linear dialkyl anion and a chelate cation[120]. It has so far been impossible to replace the lithium cation in the complex and also to use other complex-forming agents for lithium.

Perhalogenoaryl anionic complexes are entirely stable in air and in the light both in the solid state and in solution. Perchloro- and perfluoro-phenyl anionic complexes of two types are known: homoligand and heteroligand. They are readily formed at low temperatures in ether from the tetrahydrothiophen complex of gold chloride and perhalogenoaryl-lithium[121–123]. When equimolar amounts of the initial reactants are employed, heteroligand anionic complexes are formed:



while in the presence of an excess of perhalogenoaryl-lithium, homoligand anionic complexes are isolated:



Dialkylaurates react with various electrophiles under milder conditions than the corresponding neutral complexes[118,124,125]. Their protolysis and their reactions with bromine and alkyl halides have been described[118,124,125].

The protolysis of lithium ethylmethyl(triphenylphosphine)-aurate takes place readily at 0 °C on treatment of its ethereal solution with hydrogen chloride[124]. The reaction resulted in the isolation of methane, ethane, and the triphenylphosphine complexes of methyl- and ethyl-gold:

$$[MeEtAuPPh_3]^-Li^+ + HCl \rightarrow CH_4 + C_2H_6 + MeAuPPh_3 + EtAuPPh_3 + LiCl .$$

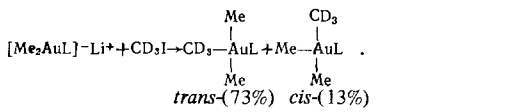
The reaction of dialkylaurates with bromine leads to a mixture of products in which the trialkylgold complex predominates[124]:

$$[Me_2AuPPh_3]^-Li^+ + Br_2 \rightarrow Me_2AuBrPPh_3 + LiBr \xrightarrow{[Me_2AuPPh_3]^-Li^+} \rightarrow Me_3AuPPh_3 + MeAuPPh_3 .$$

Under the influence of halogens and perfluoroaryl derivatives of tervalent thalium, perhalogenoaryl anionic complexes give rise to oxidative addition products[121–123]:

$$[(C_6Cl_5)_3Au]^- \xrightarrow{I_2} [(C_6Cl_5)_2AuI_2]^- .$$

The reaction of dialkylaurates with alkyl halides also proceeds via the oxidative addition mechanism[118,124,125]. The study of the stereochemistry of this reaction showed that mainly the *trans*-isomer is formed[118]:



trans-(73%) *cis*-(13%)

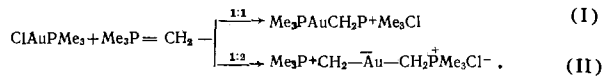
Perfluorophenylaurate reacts with bis(triphenylphosphine)-gold perchlorate, the ligand being substituted with formation of a neutral complex of perfluorophenylgold: [123]

$$[(C_6F_5)_2Au]^-Bu_4N^+ + (Ph_3P)_2Au^+ClO_4^- \rightarrow 2C_6F_5AuPPh_3 + Bu_4N^+ClO_4^- .$$

V. YLID COMPLEXES OF GOLD

The formation of extremely stable ylid complexes is characteristic of all Group IB metals[126,127]. The ylid complexes of gold, first obtained in 1973, have been investigated very vigorously in recent years. The interest in compounds of this kind is associated primarily with their unusually high thermal stability for organogold complexes. These complexes have also found applications in medicine in recent years[128].

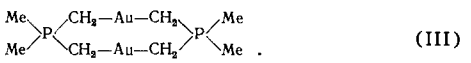
Depending on the reactant ratio, the interaction of $ClAuPMe_3$ with $Me_3P{=}CH_2$ leads to the formation of various phosphonium salts[127–130]:



(I)

(II)

In the presence of a large excess of the ylid, an eight-membered heterocyclic compound (III) with two gold atoms is obtained[127–129,131]:

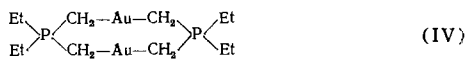


(III)

Compounds of types (I), (II), and (III) have been obtained for a series of alkylphosphines, for example for triethyl-, tributyl-, and dimethylcyclopropyl-phosphines[128,131,132] and also for triphenylphosphine ylids[130,133].

Phosphonium salts of types (I) and (II), in which the hydrogen atom of the methylene group has been substituted by the Me_3Si group, have been described[130]. As-analogues of cyclic ylid complexes have been obtained[131].

The complex

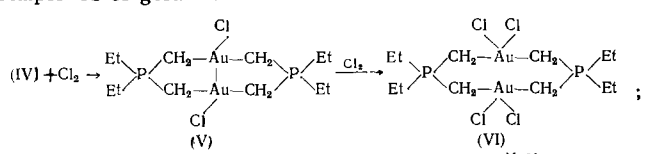


(IV)

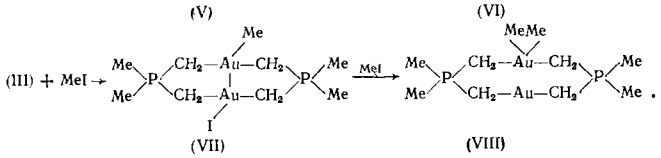
has been studied by X-ray diffraction and its Mössbauer and ESCA spectra have been investigated[134]. In complex (IV) there are two parallel linear –C–Au–C– fragments whose gold atoms hardly interact.

The ylid complexes of gold are solid substances stable in air and in the light. The thermal stability of these complexes, some of which actually sublime and distil *in vacuo* without decomposition, is unusually high[127,129,130,132].

The ylid complexes of type (III) readily undergo oxidative addition reactions under the influence of halogens and alkyl halides[129,135]. Thus, when complex (IV) was treated with chlorine, a dinuclear cyclic complex (V) was obtained, from which a gold(III) ylid complex (VI) was formed on further treatment with chlorine. Treatment of complex (III) with methyl iodide gives rise to complexes (VII) and (VIII). Complexes (V) and (VII), in which the gold atom is in the unusual oxidation state of +2 according to Mössbauer and ESCA spectroscopic data, are of special interest[134]. According to X-ray diffraction data, the Au–Au distance in complex (V) is 2.60 Å and is the smallest in all the known organic complexes of gold[135]:

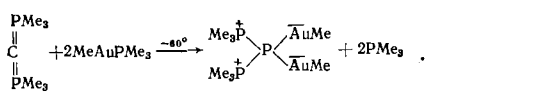


(V) (VI)



(VII) (VIII)

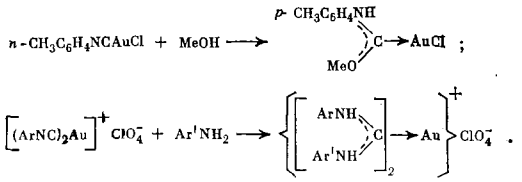
Hexamethylcarbodiphosphorane[136] reacts with two molecules of $MeAuPMe_3$ to form a complex in which the tetrahedral carbon atom is linked to two gold atoms[137]:



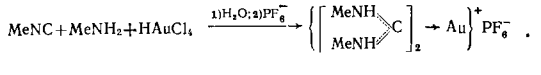
VI. CARBENE COMPLEXES OF GOLD

In 1971 two groups of investigators obtained almost simultaneously carbene complexes of gold[138,139].

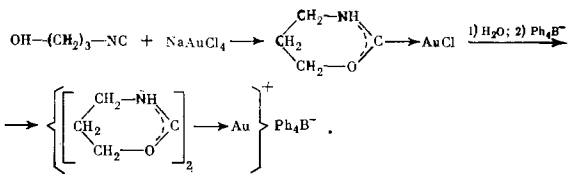
Two types of carbene complexes containing either one or two carbene ligands have been described for univalent gold. Both mono- and di-carbene complexes are formed readily from isonitrile complexes of gold in the presence of an amine or an alcohol[36,102,140–145]:



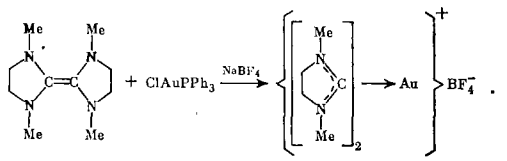
Instead of using isonitrile complexes, one can introduce into the reaction a univalent or tervalent gold salt and the isonitrile in the presence of an amine or alcohol[36,140,142]. In view of the highly nucleophilic properties of the amines, the reactions with the latter always proceed under milder conditions than with alcohols[145]:



Hydroxy-substituted isonitriles react with gold compounds to form a cyclic alkoxy(alkylamino)carbene complex[146]:

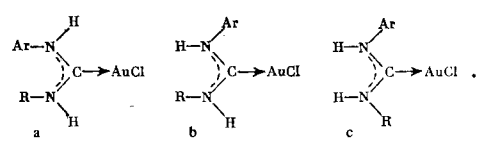


Olefins activated by electron-donating substituents are converted into carbene complexes on reaction with gold salts[147,148]:



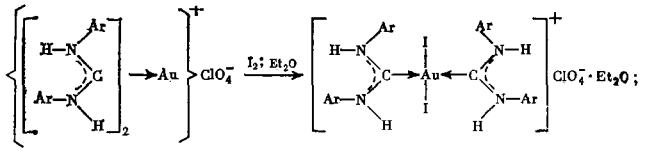
The carbene complexes of gold are white solids stable in air but sensitive to light. Some of them exhibit a luminescence of different colours and durations on irradiation with ultraviolet light[140]. This property has proved useful for the determination of the purity of the complexes. Carbene complexes with substituted tetrazoles are used in medicine as anti-inflammatory preparations[144].

Spectroscopic studies have shown that the rotation about the C–O and C–N bonds is limited, that the multiplicity of these bonds is greater than unity, and that the carbene ligand has a planar structure[142,143]. In conformity with this structure, the carbene complexes exist in the form of geometrical isomers. Among the three possible geometrical isomers a–c, isomer b predominates[142,143,145]:



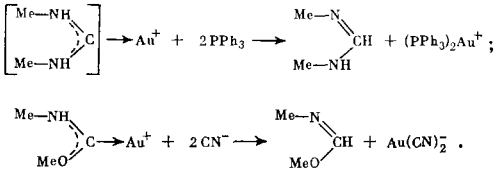
a b c

The reactivity of the carbene complexes has been little investigated. As for the majority of the organic complexes of gold, they readily undergo reactions involving oxidative addition of the halogen and ligand exchange reactions. The oxidative addition of iodine or bromine to the dicarbene complex of gold(I) leads to a dicarbene complex of gold-(III):[62,140,141,149]



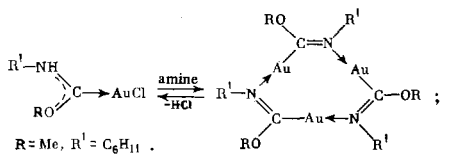
Ar = *p*-$CH_3C_6H_4$.

According to X-ray diffraction data, the tervalent gold complex is square planar with *trans*-carbene ligands[149,150]. The carbene ligand is substituted on treatment with other fairly powerful electron-donating ligands such as triphenylphosphine, cyanide, or isonitrile[140,142,145]:



It is noteworthy that the last reaction has served as a key to the explanation of the catalytic effect of added $HAuCl_4$ in reactions involving α-addition of amines to isonitriles, leading to substituted formamidines. The role of the gold salt reduces to the formation of the isonitrile complex of gold(I), which is converted into a carbene complex in which the carbene ligand is substituted by the isonitrile ligand, giving rise to a substituted formamidine and the initial isonitrile complex of gold(I).[140,142]

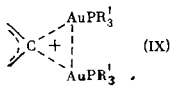
The deprotonation reaction, leading to the formation of organic σ-derivatives of gold, is specific to the carbene complexes. On treatment with bases, the deprotonation takes place with formation of cyclic trimers[36,102] (see above). This reaction is reversible and, on treatment with acid, carbene complexes are reformed from the trimer[36,102,151]:



R = Me, R' = C_6H_{11} .

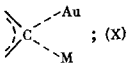
VII. ORGANOGOLD COMPOUNDS WITH A BRIDGING CARBON ATOM

Like the majority of transition metals, gold forms organometallic compounds with a metal–metal bond. The dinuclear cationic complexes $[R(AuPR'_3)_2]^+X^-$, in which the organometallic fragment (IX) of the molecule is a three-membered gold-carbon ring with an Au–Au bond and a bridging carbon atom, have been fairly thoroughly investigated[5]:



(IX)

Aryl compounds of gold in which the bridging carbon atom is linked to different metal atoms, one of which is gold and the other is zinc, copper, silver, or lithium [compounds (X)] are also known:



; (X)

M = Zn, Li, Cu, Ag .

Compounds of this type are usually dimeric and form metal–carbon macrorings—for example, triphenylgoldzinc.

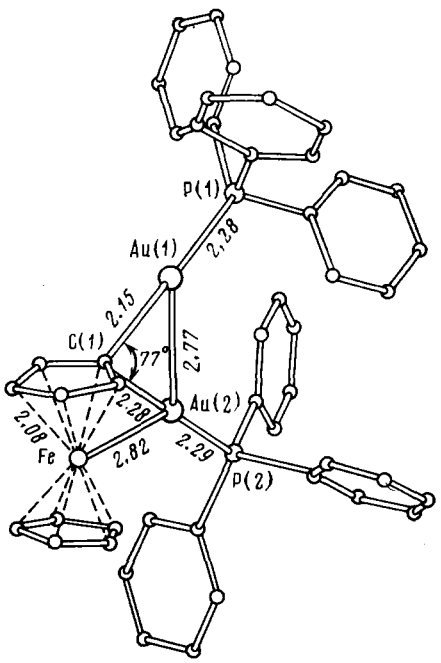
1. Homonuclear Cationic Complexes $[R(AuPR'_3)_2]^+X^-$

Dinuclear cationic complexes of type (IX) have been obtained for phenyl, ferrocenyl, cymantrenyl, and alkenyl derivatives of gold and both their structures and chemical behaviour have been studied in detail[2,5,152,153].

(a) Structure

The structures of the dinuclear cationic complexes of gold have been determined by infrared, ultraviolet, Raman, and NMR spectroscopy and also by X-ray diffraction.

The most stable ferrocenyl complex has been studied by X-ray diffraction[154,155]. It was established that the Au–Au distance in this complex (2.77 Å) is shorter than the Au–Au distance in the metal (2.88 Å), while the Au(1)–C(1)–Au(2) angle is much smaller than the tetrahedral value, which indicates the existence of a bond between the two gold atoms (see Figure). The plane of the three-membered Au(1)C(1)Au(2) ring is almost perpendicular to the plane of the cyclopentadienyl ring and the C(1) carbon atom occupies a bridging position between the two gold atoms. The interaction of C(1) with the two gold atoms must be regarded as a two-electron three-centre bond. Cluster compounds of copper and silver with a bridging ferrocenyl group have been described recently[156,157].



The structure of bis(triphenylphosphinegold)ferrocenium tetrafluoroborate.

The study of the ultraviolet and infrared spectra of the tolyl complex[158], the study of the *p*-fluorophenyl complex by ^{19}F NMR,[159] and the Raman spectroscopic study of the styryl complex[81] have shown that the aryl and alkenyl cationic complexes have a structure of type (IX), in which the carbon atom of the organic group occupies a bridging position between two gold atoms.

(b) Methods of Synthesis

From organogold compounds. When organogold complexes were treated with HBF_4, dinuclear complexes of type (IX) were obtained in high yields[2,5]:

$$RAuPR_3' + HBF_4 \rightarrow [R(AuPR_3')_2]^+BF_4^- + RH \ .$$

The cation R'_3PAu^+ can be conveniently generated from R'_3PAuCl on treatment with silver tetrafluoroborate.

From organomercury compounds. When organomercury derivatives R_2Hg are treated with phosphine complexes of methylgold in the presence of HBF_4, mercury is substituted by gold in a series of aryl, alkenyl, ferrocenyl, cymantrenyl, and heterocyclic organomercury compounds[21,22,160]. Depending on the group R in the initial organomercury derivative, various types of organogold complexes are formed. Thus treatment of diaryl- and distyryl-mercury derivatives with electron-accepting substituents in the group with phosphine complexes of methylgold and HBF_4 led to the isolation of only the organomonogold complexes[21]:

$$R_2Hg + MeAuPPh_3 \xrightarrow{HBF_4} RAuPPh_3 \ ;$$

R=X—C_6H_4, where X=*p*-, *m*-COOEt, *o*-I; PhCH=C(COOMe).

Cationic dinuclear complexes are formed from diferrocenylmercury derivatives having both electron-donating and electron-accepting substituents, from distyryl-, dicymantrenyl-, and dithienyl-mercury, and also from diaryl compounds of mercury having electron-donating substituents in the aromatic ring[21,22,160]:

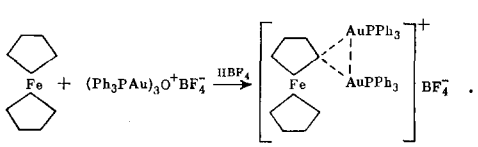
$$R_2Hg + MeAuPPh_3 \xrightarrow{HBF_4} [R(AuPPh_3)_2]^+BF_4^- \ ;$$

R=X—$C_5H_4FeC_5H_4$, where X=H; Cl; Br, OMe, COOMe; Y—C_6H_4, where Y=H, Me, NH_2.

A characteristic feature of *p*-halogenoarylmercury derivatives is that, by altering the reaction conditions, it is possible to obtain from them both dinuclear gold complexes and organomonogold compounds[21].

It is noteworthy that organogold complexes having the same geometrical configuration as the initial organomercury compound have been obtained from the *trans*-isomers of alkenyl derivatives of mercury[22,81].

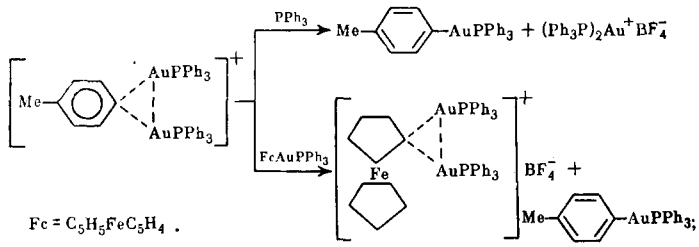
Substitution of gold in ferrocene and its derivatives. Ferrocene and its derivatives react with tris(triphenylphosphinegold)oxonium tetrafluoroborate at room temperature in the presence of HBF_4 to form dinuclear cationic complexes[161,162]:



The preferential formation of homoannular substituted compounds on substitution of gold in chloro-, bromo-, methoxy-, acetyl- and nitro-ferrocenes is apparently caused by the additional stabilisation of the cationic centre in the 1,2-isomer by the coordination of the gold atom to the substituent[162].

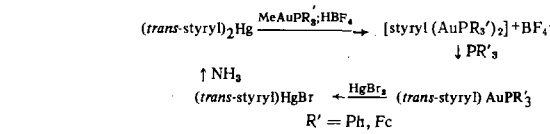
(c) Reactions

The study of the chemical behaviour of dinuclear organogold compounds has shown that reactions of two types are characteristic of these compounds—those involving only one or both $AuPR'_3$ groups. The first type involves the striking ability of the complexes $[R(AuPr'_3)_2]^+BF_4^-$ to enter into various reactions involving the transfer of the $R'_3PAu_3^+$ cation. The reaction proceeds readily under the influence of nucleophiles such as phosphines, amines, and halide ions. Another organogold compound can also fulfil the role of the nucleophile[2,5]:



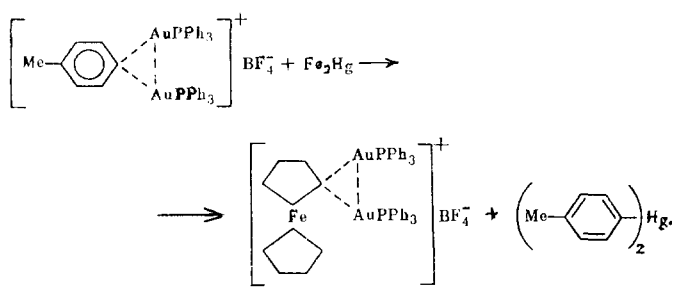
A feature of the reactions of alkenyl dinuclear complexes should be noted. Thus the dinuclear cationic complex obtained from the triphenylphosphine complex of *trans*-styrylgold generates, under the influence of triphenylphosphine or ferrocenylgold, an organomonogold compound having the same geometrical configuration as that of the initial *trans*-styrylgold[81].

A series of reactions, illustrated schematically below, have been carried out for *trans,trans*-distyrylmercury[81]:



An analogous sterochemical result has also been obtained for *trans,trans*-di(1-methoxycarbonyl-2-phenylvinyl)mercury[22].

The reactions of the cationic complexes with organometallic compounds belong to the second type. Thus the interaction of the cationic tolyl complex with diferrocenylmercury results in the formation of ditolylmercury and a dinuclear ferrocenylgold complex in high yields[2,19]:



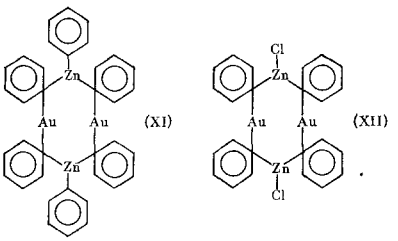
The mild reaction conditions and the high yields of products make it possible to use the dinuclear cationic complexes of gold for the synthesis of new organogold complexes with different organoelemental ligands, including gold-containing ligands.

2. Heterometallic complexes of arylgold

Heterometallic cluster complexes of arylgold of type (X) have been described by two groups of Dutch investigators.

De Graaf and coworkers[163,164] obtained aryl complexes containing gold and zinc; Van Koten and coworkers[39,165-167] investigated arylgold complexes containing also lithium, silver, or copper atoms.

Triphenylgoldzinc was isolated after treating diphenylzinc with an ethereal solution of $AuCl_3$ or AuCl(CO).[163] The compound is dimeric in benzene; since it has a dipole moment close to zero, a dimeric structure (XI) was attributed to it. ^1H and ^{13}C NMR data also agree with the dimeric structure. If diphenylzinc and AuCl(CO) react in proportions of 1 : 1, a compound having the composition $Ph_2AuZnCl$ is formed, for which structure (XII) has been proposed. Here the phenyl groups at the zinc atom have been substituted by chlorine atoms:



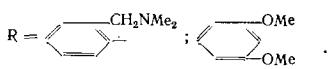
Whereas triphenylgoldzinc is extremely sensitive to atmospheric moisture, its chlorine-containing analogue is much more stable.

Analogues of compounds (XI) and (XII) have been obtained for *p*-ditolylzinc, whereas for other arylzinc derivatives with electron-donating substituents, only complexes of type (XII) have been isolated[164]. Organozinc and organogold compounds are known to form the most stable complexes with nitrogen- and phosphorus-containing ligands respectively. Accordingly, the reaction of triphenylgoldzinc with bipyridyl and tetramethylethylenediamine gives rise to complexes via the zinc atom, while the interaction with triphenylphosphine and diphos leads to phosphine complexes of phenylgold[164]:

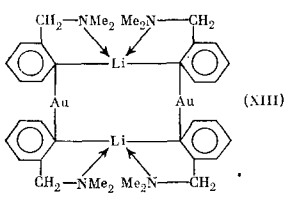
$$XI \xrightarrow{(C_5H_4N)_2} 2Ph_3AuZn\cdot(C_5H_4N)_2$$
$$XI \xrightarrow{PPh_3} 2Ph_2Zn + 2PhAuPPh_3 .$$

The triphenylphosphine complexes of arylgold or gold bromide react with aryl-lithium compounds to form mixed Au–Li clusters with bridging aryl groups[38]:

$$(RLi)_4 + BrAuPPh_3 \rightarrow R_4Au_2Li_2 ;$$

$R =$  ;

Bis[2-(dimethylaminomethyl)phenyl]goldlithium is a dimeric compound thermally stable up to 170 °C; structure (XIII) has been proposed for it[4,38]:



This mixed Au–Li cluster has served as the starting material for the synthesis of a stable phenyl derivative of univalent gold, existing without an external stabilising ligand—(2-dimethylaminomethyl)phenylgold[38] (see above). In addition, other cluster complexes of gold have been obtained from compound (XIII). Thus the reaction of compound (XIII) with copper(II) bromide led to the isolation in a high yield of a dimeric (in benzene) cluster containing gold and copper atoms[165,166]:

$$R_4Au_2Li_2 + 2CuBr \rightarrow R_4Au_2Cu_2 + 2LiBr .$$

The reaction of compound (XIII) with $(CF_3SO_3)Cu$ and $(CF_3SO_3)Ag$ yielded new hexanuclear clusters containing gold and copper and gold and silver respectively[167]:

$$R_4Au_2Li_2 + (CF_3SO_3)M \rightarrow R_4M_1Au_2(CF_3SO_3)_2 ;$$
$$M = Cu, Ag .$$

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The Oxidation-reduction Reactions of Gold Complexes

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The review deals with reactions involving oxidative addition to both organogold compounds and to gold complexes without Au-C bonds. Furthermore, the review includes reactions involving the reductive elimination of alkyl groups from tervalent gold complexes.
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I. INTRODUCTION

The oxidation addition reactions constitute one of the types of reactions characteristic of organometallic σ-compounds of transition metals. The most familiar reagents capable of oxidative addition are halogens, alkyl halides, and alkyl disulphides. However, the range of these compounds is being continually expanded. Oxidative addition is nowadays regarded as one of the stages in the protolysis of certain organometallic compounds by hydrogen halides.

Despite the fact that the oxidative addition reactions are known for derivatives of many metals, their characteristics are by no means clear. The most convenient objects for the investigation of these reactions are compounds of gold and platinum group metals. This is due to the fairly high stability of the organometallic σ-derivatives of these elements and also the simplicity with which the stereochemistry of the process can be followed.

This review is devoted to reactions of organogold compounds of the oxidative addition type. The reductive elimination processes can be logically related to the former reactions and are also considered in the present review.

Apart from its general theoretical importance, the study of reactions involving oxidative addition to gold(I) complexes is also important from the preparative standpoint, because gold(I) compounds are much more readily available than gold(III) compounds.

II. OXIDATIVE ADDITION REACTIONS

1. Reactions Involving Oxidative Addition to Complex Salts LAuX

When phosphine[1-5] and arsine complexes[3] of univalent gold halides react in polychlorohydrocarbons with an excess of the halogen of the same type as in the halide, gold trihalide complexes are formed in high yields:

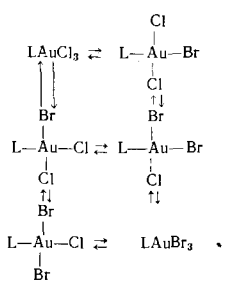
$$R_3PAuX + X_2 \rightarrow R_3PAuX_3 ;$$
$$X = Cl, Br, \text{or } I;\ R = Et,\ Ph,\ \text{cyclo-}C_6H_{11},\ \text{or } C_5H_5FeC_5H_4;$$
$$Ph_3AsAuCl + Cl_2 \rightarrow Ph_3AsAuCl_4 .$$

A mixture of ethanol and tetrahydrofuran can also be used as the solvent[3]. The infrared spectra of the complexes have been investigated[6].

The same product is formed in the reactions of Et_3PAuBr with iodine and of Et_3PAuI with bromine in equimolar amounts. This result was initially explained by the high mobility of the halogens in $Et_3PAuBrI_2$ and Et_3PAuBr_2I and by the formation of the more stable of the above two compounds in both reactions[1]. However, later investigations by NMR showed[7,8] that the process involves the formation of a mixture of all possible complexes of the type $LAuX_aY_{3-a}$ with an approximately statistical distribution of the halogens X and Y. Thus, for the reaction

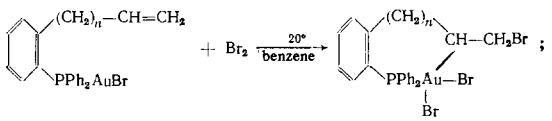
$$Et_3PAuBr + Cl_2 \xrightarrow[h\nu]{25^\circ} Et_3PAuBr_{3-a}Cl_a ;$$
$$a = 0,\ 1,\ 2,\ 3 .$$

the following equilibrium states have been discovered[8]:



Deviations for the statistical distribution of the halogen atoms in this reaction have been observed only for complexes with a large amount of bromine—$LAuClBr_2$ and $LAuBr_3$.[8] The behaviour of the univalent gold in this reaction is analogous to that of the isoelectronic platinum(II) complexes Br_aCl_{4-a}. $.PtL_2$, for which a statistical distribution of halogen atoms has also been observed[9].

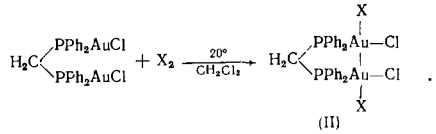
When the phosphine complexes of AuBr in which the ligand contains C=C double bonds are treated with bromine, organic derivatives of tervalent gold are formed as a result of the addition of gold to the double bond[10]:



$n = 0$ or 1. (I)

The structure of the resulting yellow crystalline compounds (I) has been determined by X-ray diffraction[10]. In both compounds (I) the gold atom has the square planar environment characteristic of gold(III). The five-membered ring in compound (I) ($n = 0$) has the envelope conformation, while the six-membered ring in compound (I) ($n = 1$) has the twist-boat conformation. The Au–C bond in compounds (I) persists also in solutions (according to ^1H NMR data).[10]

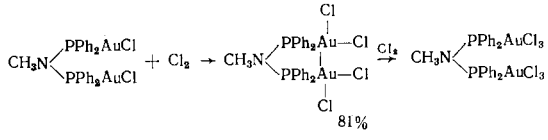
The reaction with halogens of AuCl complexes containing bidentate phosphine ligands and in which two gold atoms are in close proximity in space can lead to the formation of gold compounds with a formal oxidation state +2. Thus the reaction of equimolar amounts of a halogen and the complex of AuCl with bis(diphenylphosphino)methane leads to the formation of compound (I):[11]



(II)

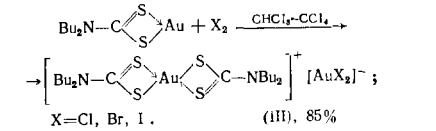
$Me_2C(PPh_2AuCl)_2$ reacts analogously with chlorine and bromine. The reaction involving $H_2C(PPh_2AuI)_2$ with iodine leads to an unstable complex $H_2C(PPh_2AuI)_2.I_2$, which readily loses iodine *in vacuo* or on recrystallisation. Infrared, ^{197}Au Mössbauer, and X-ray electron spectroscopic data have shown that the oxidation state of the gold in complexes (II) is intermediate between +1 and +3.[11]

When compound (II) is treated with an excess of a halogen, the tervalent gold complexes $H_2C(PPh_2AuClX_2)_2$ are formed. Analogous reactions have been performed for another bisphosphine complex[12]:



81%

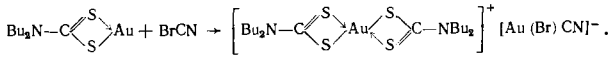
The reactions of halogens with other gold salts have been much less thoroughly investigated. When gold butylthiocarbamate is treated with halogens, the products are either the tervalent gold compound $Bu_2NCS_2AuBr_2$ [13,14] or salt-like complexes containing both Au(I) and Au(III):[15]



X=Cl, Br, I. (III), 85%

The structure of the bromide (III) has been established by X-ray diffraction (the tervalent gold atom has a square planar environment)[15].

An analogous compound has been obtained on treatment with bromocyanogen[15]:



The reactions of arsine and phosphine complexes of gold salts with tervalent thallium compounds have been studied in greater detail. Thus, when triphenylphosphinegold chloride and $TlCl_3$ are refluxed in chloroform, a gold trichloride complex is formed in 95% yield[16]:

$$Ph_3PAuCl + TlCl_3 \rightarrow Ph_3PAuCl_3 + TlCl\ .$$

The reaction of LAuX with bis(pentafluorophenyl)thallium halides in benzene leads to bis(pentafluorophenyl)gold halides[17–20]:

$$LAuX + (C_6F_5)_2TlZ \rightarrow (C_6F_5)_2Au(X)L + TlZ\ ;$$
$$L=PPh_3,\ AsPh_3;\ X=Cl,\ Br,\ I;\ Z=Br,\ I\ ;$$
$$[-CH_2PPh_2AuCl]_2 + (C_6F_5)_2TlBr \rightarrow [-CH_2PPh_2Au(C_6F_5)_2Cl]_2\ .$$

It has been established for bis(pentafluorophenyl)gold chloride that the C_6F_5 groups are in the *cis*-positions relative to one another[17]. The isonitrile complex of AuCl reacts analogously[21]:

$$PhNCAuCl + (C_6F_5)_2TlBr \xrightarrow[benzene]{80°;1.5\ h} PhNCAu(C_6F_5)_2Cl + TlBr\ .$$

The reaction of t-BuNCAuCl yields a mixture of products which are difficult to separate[21].

Pentachlorophenylthallium(III) compounds can function as oxidants in relation to gold complexes, but in this case a complex of univalent gold is formed together with the gold(III) compound:

$$Ph_3PAuCl + (C_6Cl_5)_2TlCl \xrightarrow{-TlCl} (C_6Cl_5)_2Au(Cl)PPh_3 + C_6Cl_5AuPPh_3\ .$$

This result has been explained by the lower oxidising capacity of $(C_6Cl_5)_2TlCl$ compared with that of pentafluorophenyl derivatives of thallium[22].

When Ph_3PAuCl reacts with a fully substituted organic compound of thallium(III), oxidation is not observed at all and only a gold(I) compound is formed[23]:

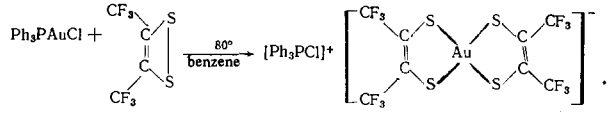
$$Ph_3PAuCl + (C_6HCl_4)_3Tl \xrightarrow{CHCl_3} Ph_3PAuC_6HCl_4\ .$$

In contrast to complexes of univalent gold halides, the triphenylphosphine complexes of gold(I) nitrate, perchlorate, acetate, and thiocyanate react with perfluorophenylthallium compounds to form only univalent gold derivatives[19]:

$$Ph_3PAuZ + (C_6H_5)_2TlX \rightarrow Ph_3PAuC_6F_5\ ;$$
$$Z=NO_3,\ ClO_4,\ CH_3COO,\ SCN,\ X=Br,\ I\ .$$

The causes of the difference between the reactivities of gold halides and those of other gold(I) salts are not discussed in the literature, but the differences agree satisfactorily with the greater ease of reductive elimination in the compounds $LAuR_2Z$ for $Z = NO_3$ or ClO_4 compared with Z = halogen (see below).

The reaction of triphenylphosphinegold chloride with the disulphide $(CF_3)_2C_2S_2$ has been described[24]. During the reaction, the phosphine ligand is displaced and an anionic complex of tervalent gold is formed, its structure having been established by X-ray diffraction[25]:



The gold atom in the anion of this complex has a square planar coordination and the S...S distances are 3.23 Å.

2. Reactions Involving Oxidative Addition to the Aurates $M^+[Au(X)Y]^-$

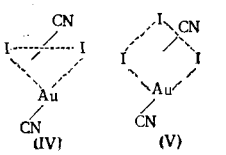
When a slight excess of halogens is allowed to act on potassium dicyanoaurate in H_2O-CH_3OH, tervalent gold aurates are formed[26–29]:

$$K[Au(CN)_2] + X_2 \rightarrow trans\text{-}K[Au(CN)_2X_2]\ ;$$
$$X=Cl,\ Br,\ I\ .$$

The infrared spectra of the compounds obtained have been studied in detail[27,28] and it has been shown that the reaction involves *trans*-addition.

It has been observed that the addition of iodine is greatly accelerated in the presence of the iodide ion[30]. This effect has been explained by the preferential *trans*-disposition of iodine atoms in the transition state of the reaction with I_3^-

compared with the addition of I_2 [cf. the transition states (IV) and (V)]:



(IV) (V)

Oxidative addition products have been obtained by treating with alkyl bromides or iodides the dialkylaurates(I), which are readily obtained when phosphine complexes of alkylgold-(I) are acted upon by alkyl-lithium compounds. In the resulting tervalent gold compounds two methyl groups are in the *trans*-positions relative to one another[31,32]. The yields of gold(III) complexes range from 30 to 70%:

$$Li^+[Me_2AuPPh_3]^- + RX \rightarrow R{-}AuMe(PPh_2) + LiX ;$$

R=Et, Bu, iso-Bu; X=Br, I ;

$$Li^+[R(Me)AuPPh_3]^- + MeI \rightarrow R{-}AuMe_2PPh_3 + LiI ;$$

R = iso-Pr, t-Bu, or noe-C_5H_{11};

$$Li^+[Me_2AuPPh_3]^- + CD_3I \xrightarrow{LiI} \underset{73\%}{CD_3{-}AuMe_2PPh_3} + \underset{13\%}{Me{-}AuMe_2PPh_3} .$$

If the phenyl group is present in the gold(III) compound obtained, then the compound has the *cis*-configuration[31,32]:

$$\left.\begin{array}{l} Li^+[Me_2AuPPh_3]^- + PhI \\ Li^+[Ph(Me)AuPPh_3]^- + MeI \end{array}\right\} \rightarrow Me{-}AuMePhPPh_3 + LiI .$$

When equimolar amounts of bromine and lithium dimethylaurate react, a mixture of methyl derivatives of univalent and tervalent gold is formed, probably as a result of the following reactions[32]:

$$Li^+[Me_2AuPPh_3]^- + Br_2 \rightarrow Me_2Au(Br)PPh_3 + LiBr ;$$

$$Li^+[Me_2AuPPh_3]^- + Me_2Au(Br)PPh_3 \rightarrow Me_3AuPPh_3 + MeAuPPh_3 + LiBr .$$

In contrast to dimethylaurate, the mixed complex (VI) is converted into gold(III) compounds in high yields on treatment with bromine or bis(pentafluorophenyl)thallium bromide[33]:

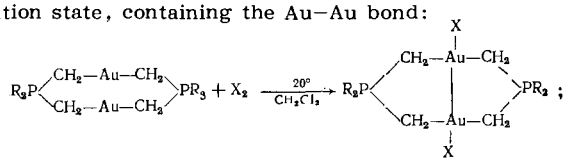
$$Bu_4N^+[C_6F_5AuBr]^- \xrightarrow{Br_2} \underset{65\%}{Bu_4N^+[C_6F_5AuBr_3]^-}$$

$$Bu_4N^+[C_6F_5AuBr]^- \xrightarrow{(C_6F_5)_2TlBr} \underset{90\%}{Bu_4N^+[(C_6F_5)_3AuBr]^-} .$$

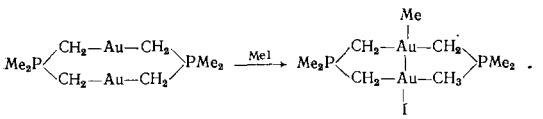
(VI)

Thus the oxidative addition of univalent gold to aurates constitutes a convenient and promising method of synthesising organic derivatives of tervalent gold.

Reactions involving the oxidative addition of halogens[34-36] and methyl iodide[36] have also been achieved for close analogues of dialkylaurates—the ylid complexes of gold. The spatial proximity of the gold atoms in these dinuclear complexes and their structural rigidity permit in this instance the formation of gold compounds (VII), with a formal +2 oxidation state, containing the Au–Au bond:



R = Me, or Et, X = Cl, Br, or I, (VII), 36—85%

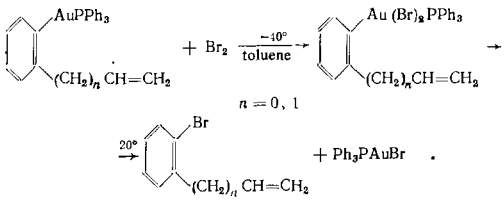


When gold(II) complexes are acted upon by an excess of halogen or MeI, they are converted into tervalent gold compounds.

The presence of the transannular Au–Au bond in compound (VII) has been demonstrated by an X-ray diffraction study of compound (VII, X = Cl), in which the distance between the gold atoms is 2.597 Å.[34] In the initial ylid complex of univalent gold the Au...Au distance is 3.023 Å.[37]

3. Reactions Involving Oxidative Addition to the Polyhalogenoaryl Compounds $C_6X_nH_{5-n}AuL$

The Au–C bond in the aryl and the similar ferrocenyl organogold compounds $RAuPR'_3$ is readily ruptured by halogens with formation of $R'_3PAuHal$.[38-41] Unstable oxidative addition products have been detected only in the reaction of *o*-vinylphenyl- and *o*-allylphenyl-(triphenylphosphine)gold with bromine[42]:



$n = 0, 1$

However, the gold(III) complexes have been fairly poorly characterised.

On the other hand, the polyhalogenoaryl compounds of gold(I) are readily converted into gold(III) complexes on treatment with halogens, thallium trichloride, and methyl iodide.

The reaction with halogens[16,20,21,43-46] leads to the formation of the corresponding dihalides (VIII):

$$C_6X_5AuL + Hal_2 \xrightarrow[CCl_4 \text{ or } CH_2Cl_2]{0^\circ} C_6X_5Au(Hal)_2L ;$$

(VIII), 34—85%

X = F, Cl, or Br; Hal = Cl, Br, or I, L = PEt_3, or PPh_3, $AsPh_3$, PhNC, or RNH—C—R' .

The *trans*-configuration of the coordination environment of gold has been demonstrated for the dichloride (VIII).[21,44-46] The *trans*-dihalides (VIII) are readily converted into the *cis*-isomers on heating[16,45,46].

The formation of the products of the cleavage of the C–Au bond on treatment with halogens has been observed only for the perfluorophenyl compounds[16,43-45]. The proportions of the products of the oxidative addition and of the cleavage of the C–Au bond depend on the nature of both the halogen and of the stabilising ligand L. For $C_6F_5AuPPh_3$, the amount of the oxidative addition product increases in the sequence Cl < Br < I, while the opposite sequence holds for C_6F_5AuAs. Ph_3: I < Br < Cl.[45] However, the C–Au bond cannot be ruptured by halogens even in the perfluorophenyl derivative of gold when the ligand is phenylisonitrile[21].

Refluxing of C_6X_5AuL in chloroform in the presence of $TlCl_3$ also leads to $C_6X_5AuCl_2L$, but in this case the *cis*-isomer is formed:

$$C_6X_5AuL + TlCl_3 \xrightarrow{CHCl_3} \underset{60-90\%}{cis\text{-}C_6X_5Au(Cl)_2L} + TlCl ;$$

L = PEt_3, PPh_3, or $AsPh_3$; X = F 16, Cl 16, 44, 46, or Br 45.

The complexes of ethyl- and phenyl-gold do not give rise to gold(III) compounds under these conditions[16]:

$$RAuPPh_3 + TlCl_3 \rightarrow Ph_3PAuCl + TlCl\ ;\quad R = Et, \text{ or } Ph.$$

The reaction of pentachlorophenyl(triphenylarsine)gold with methyl iodide[44], leading to a mixture of isomeric gold(III) complexes, has been achieved:

$$C_6Cl_5AuAsPh_3 + MeI \rightarrow \underset{60\%}{C_6Cl_5\,(Me)\,Au\,(I)\,AsPh_3}\ .$$

$C_6F_5AuAsPh_3$ also reacts with methyl iodide, but the products of this reaction have not been determined[44].

Thus reactions involving oxidative addition to polyhalogenoaryl compounds of univalent gold constitute a convenient method of synthesising the corresponding gold(III) complexes.

4. Reactions Involving Oxidative Addition to the Alkyl Complexes RAuL

The reactions of methylgold complexes with MeI and CF_3I have been studied in fair detail. The first studies on this problem showed that the reaction of methyl(triphenylphosphine)gold with methyl iodide in benzene or in MeI at 20 to 25 °C leads to ethane and a gold iodide complex[47,48]:

$$MeAuPPh_3 + MeI \rightarrow C_2H_6 + Ph_3PAuI;$$
$$[-CH_2P\,(Ph)_2\,AuMe]_2 + MeI \rightarrow [-CH_2P\,(Ph)_2\,AuI]_2 + C_2H_6\ .$$

Methyl iodide reacts analogously with silicon-containing derivatives of univalent gold[47]:

$$Ph_3PAuCH_2SiMe_3 + MeI \rightarrow Ph_3PAuI + Me_3SiEt\ ;$$
$$Ph_3PAuOSiMe_3 + MeI \rightarrow Ph_3PAuI + MeOSiMe_3\ .$$

NMR study of the interaction of methyl iodide with phosphine complexes of methylgold[48,49] as well as kinetic data[50] have shown that the reaction is a multistage process, the first two stages [(1) and (2)] being rapid:

$$MeAuL + MeI \rightarrow Me_2Au\,(I)\,L\ ; \quad (1)$$
$$Me_2Au\,(I)\,L + MeAuL \rightleftarrows Me_3AuL + LAuI\ ;\quad L = PMe_3,\ PMe_2Ph,\ PMePh_2 \text{ or } PPh_3. \quad (2)$$

Reaction (2), which leads to a complex of trimethylgold, is analogous to the exchange of methyl groups between platinum and gold compounds[7]:

$$cis\text{-}Pt\,(Me)_2\,L_2 + LAuBr \rightleftarrows trans\text{-}PtBr\,(Me)\,L_2 + MeAuL\ .$$

The subsequent fate of the Me_3AuL formed in reaction (2) depends greatly on the nature of the ligand L. For L = PPh_3, reductive elimination of ethane and subsequent interaction of $MeAuPPh_3$ with methyl iodide take place:

$$Me_3AuL \rightarrow C_2H_6 + MeAuL\ . \quad (3)$$

The overall result is thus the formation of methane and of a gold iodide complex.

However, the triphenylphosphine complex of trimethylgold can be isolated with a high yield when the reaction is carried out at 0 °C:[48]

$$MeAuPPh_3 + MeI \xrightarrow[0°,\ 6\ days]{\text{in soln. in MeI}} \underset{87\%}{Me_3AuPPh_3} + Ph_3PAuI\ .$$

The complexes of trimethylgold with ligands such as PMe_3 and PMe_3Ph are more stable than Me_3AuPPh_3 and equilibrium (2) shifts towards the formation of the oxidative addition product via the reaction of MeAuL with an excess of methyl iodide [reaction (1)]. Thus a complex of dimethylgold iodide has been obtained in a high yield from the trimethylphosphine complex[49]:

$$MeAuPMe_3 + MeI \xrightarrow[20°,\ 3\ weeks]{\text{in soln in MeI}} cis\text{-}Me_2Au\,(I)\,PMe_3\ .$$

When L = $PMePh_2$, a mixture of products is formed as a result of reactions (1)–(3).[50]

The mechanism of the interaction of methyl iodide with methylgold complexes discussed above is consistent with the higher rate of formation of butane compared with the rates of formation of ethane and propane on interaction of MeI with an ethylgold complex[48]:

$$EtAuPPh_3 + MeI \rightarrow C_4H_{10} + C_3H_7 + C_2H_6 + Ph_3PAuI\ .$$

However, the cause of the decomposition of the trialkylgold complex [reaction (3)] is not clear, since it is known that the complex Me_3AuPPh_3 is fairly stable at 20–25 °C.[51] It may be that the elimination of ethane is in this instance catalysed by methyl iodide[48].

Trifluoroiodomethane reacts with MeAuL similarly to methyl iodide[49,52]. In this case, when L = PMe_3 or PMe_2Ph, the isomeric complexes (IX) are formed in high yields:

$$MeAuL + CF_3I \rightarrow Me_2Au\,(CF_3)\,L + LAuI\ ;\quad L = PMe_3,\ PMe_2Ph\ (IX). \quad (4)$$

Reaction (4) in methylene chloride leads to *trans*-(IX), while in CF_3I the product is *cis*-(IX). In other solvents (ether, acetone) a mixture of the *cis*- and *trans*-isomers is formed[49].

The triphenylphosphine complex reacts with trifluoroiodomethane differently[52]:

$$MeAuL + CF_3I \rightarrow CF_3AuL + MeI\ ;\quad L = PPh_3\ . \quad (5)$$

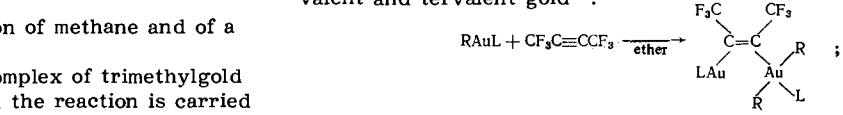
When L = $PMePh_2$ a mixture of products corresponding to reactions (4) and (5) is formed[52].

The inhibiting influence of a radical trapping agent (galvinoxyl) on reaction (4) has been observed and a radical mechanism of the formation of compound (IX) has been proposed on this basis[52]:

$$CF_3^{\cdot} + MeAuL \rightarrow [MeAu\,(CF_3)\,L]^{\cdot} \xrightarrow{CF_3I} Me\,(CF_3)\,Au\,(I)\,L + CF_3^{\cdot}\ ;$$
$$Me\,(CF_3)\,Au\,(I)\,L + MeAuL \rightarrow Me_2Au\,(CF_3)\,L + LAuI\ .$$

The poor reproducibility of the kinetic data has also been adduced as an argument in support of the radical reaction mechanism. However, the intermediate paramagnetic bivalent gold compound (X) was not detected and the authors[52] do not consider the radical mechanism to be the only one possible.

An unusual example of oxidative addition is provided by the reaction of hexafluorobut-2-yne with complexes of methyl- and ethyl-gold. This results in the formation of the dinuclear organogold compounds (XI), containing both univalent and tervalent gold[53]:



R = Me, or Et; L = PMe_3, PMe_2Ph, or $PMePh_2$. (XI), 40–77% .

The groups R in compounds (XI) are in the *trans*-positions relative to one another. In the case of $MeAuPMe_3$ the *cis*-isomer is formed in addition to the *trans*-isomer. On interaction with hexafluorobut-2-yne, the triphenylphosphine complex $MeAuPPh_3$ yields the dinuclear organogold compound $Ph_3PAuC(CF_3)=C(CF_3)AuPPh_3$, which does not contain tervalent gold[54,55]. There are data indicating a radical mechanism of the reaction of hexafluorobut-2-yne with alkoxygold complexes[53].

Thiophenol[56] and selenophenol[57] react with methylgold complexes without the formation of gold(III) compounds:

$$MeAuL + PhSH \rightarrow CH_4 + PhSAuL\ ;$$
$$L=PMe_3,\ PMePh_2 \text{ or } PPh_3;$$
$$MeAuPMe_2Ph + PhSeH \rightarrow PhSeAuPMe_2Ph\ .$$

The reactions have a radical mechanism. Compounds containing the P–H and As–H bonds react analogously and polymeric products are obtained[57]:

$$MeAuPMe_2Ph + Ph_2ZH \rightarrow (AuZPh_2)_x\ ;$$
$$Z = P, \text{or As.}$$

III. REDUCTIVE ELIMINATION FROM TERVALENT GOLD COMPOUNDS

One of the factors determining the result of the interaction of univalent gold compounds with reagents capable of oxidative addition is the thermal stability of the resulting gold(III) complex, which is directly related to the possibility of reductive elimination.

Hitherto reductive elimination had been studied virtually only for alkylgold(III) complexes. This process, which leads to the formation of a univalent gold compound, has been known for a fairly long time for organogold compounds without stabilising ligands[58]:

$$RAuX_2 \rightarrow RX + AuX\ ;$$
$$R_2AuX \rightarrow AuX + \text{hydrocarbons.}$$

The compounds *cis*-$[Me_2AuL_2]ClO_4$ are fully stable at 20 °C in the solid state, but decompose rapidly with formation of ethane at an elevated temperature, particularly in solution (under the conditions of the study of the ^1H NMR spectrum):[59]

$$\underset{\text{(XII)}}{\textit{cis}\text{-}[Me_2AuL_2]ClO_4} \xrightarrow{CHCl_3} C_2H_6 + [L_2Au]ClO_4;\quad L=PPh_3,\ AsPh_3,\ SbPh_3\ .$$

It is significant that methane is not formed under these conditions even in trace amounts.

A necessary condition for the ready occurrence of the reductive elimination reaction involving complexes (XII) was believed to be the presence of bulky ligands L. Thus *cis*-$[Me_2Au(PMePh_2)_2]ClO_4$ is stable under conditions where its triphenylphosphine analogue decomposes[59]. However, it was shown later that the oxidative addition reactions are facilitated while reductive elimination is hindered for alkylgold complexes and the isoelectronic platinum complexes with increase of the electron density at the metal atom[60,61].

The rate of elimination of two methyl groups in the complexes *cis*-$Me_2Au(X)L$ depends on the nature of X and increases in the sequence $Cl < CF_3COO < NO_3 < CF_3SO_3$.[62]

The reductive elimination in trialkylgold complexes has been studied in greatest detail. Thus, when the complex Me_3AuPPh_3 is heated to 120 °C in xylene, biphenyl, or in the absence of a solvent, ethane is eliminated[51]:

$$Me_3AuPPh_3 \xrightarrow[87\%]{120^\circ} C_2H_6 + MeAuPPh_3\ .$$

Further decomposition of the univalent gold complex takes place at a higher temperature.

In the presence of free triphenylphosphine, the rate of elimination of two alkyl groups from R_3AuPPh_3 diminishes. It is therefore believed[63] that the reductive elimination is preceded by the dissociation of the complex [reaction (6)]:

$$R_3AuPPh_3 \rightleftarrows R_3Au + PPh_3\ . \qquad (6)$$

Further decomposition of trialkylgold can take place both intramolecularly and intermolecularly, which has been demonstrated in the study of the thermolysis of an equimolar mixture of Me_3AuPPh_3 and $(CD_3)_3AuPPh_3$ at 80 °C.[64] In non-coordinating solvents (decalin, chlorobenzene, and dibutyl ether) the ratio of the C_2H_6, CH_3CD_3, and C_2D_6 formed is nearly statistical, which indicates the occurrence of the intermolecular elimination process, probably via a dinuclear intermediate of type (XIII):

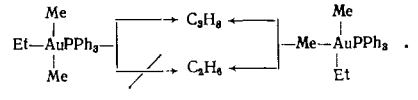
$$Me_3AuPPh_3 \rightleftarrows Me_3Au + PPh_3\ ;$$
$$Me_3Au + (CD_3)_n AuPPh_3 \rightleftarrows Me_3Au(CD_3)_n AuPPh_3\ ;$$
$$n = 1 \text{ or } 3; \qquad \text{(XIII)}$$
$$\text{(XIII)} \rightarrow MeAuPPh_3 + CD_3AuPPh_3 + C_2H_6 + C_2D_6 + CH_3CD_3\ .$$

In solvents such as dimethylformamide and dimethyl sulphoxide the cross-product CH_3CD_3 is formed only in trace amounts, which indicates intramolecular elimination. In this case the dissociation stage (6) is apparently followed by the coordination of the alkyl derivative of gold(III) to the solvent Sol:[64]

$$Me_3Au + Sol \rightleftarrows Me_3Au\cdot Sol\ ;$$
$$Me_3Au\cdot Sol \rightarrow MeAu\cdot Sol + C_2H_6, \text{ etc.}$$

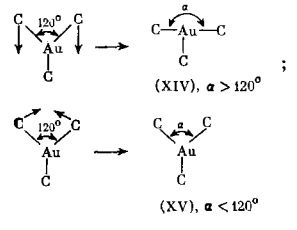
Intramolecular and intermolecular elimination pathways have also been observed in the thermolysis of $CD_3(Me)_2AuPPh_3$.[64] Apart from the nature of the solvent, the character of the process is strongly influenced also by the concentration of the gold(III) complex; with increase of concentration, the contribution of intermolecular elimination also increases.

Under the conditions of intramolecular elimination, the two alkyl groups in the *cis*-positions relative to one another are split off[63,64]. Thus the thermolysis of *trans*-$Et(Me_2)AuPPh_3$ leads mainly to the formation of propane, while the decomposition of the *cis*-isomer results in the formation of ethane and propane in comparable amounts:



The relative ease of elimination depends on the nature of the alkyl group. Thus methyl groups are eliminated with greater difficulty than ethyl groups[48], which agrees with the greater strength of the bond between the metal and the primary carbon atom.

A quantum-chemical calculation on the transition state in the reaction involving reductive elimination from a trimethylgold complex has been performed[64]. In the trimethylgold formed on dissociation of Me_3AuPPh_3 the highest occupied $4e'$ orbital is doubly degenerate if Me_3Au has the C_{3h} symmetry (the C–Au–C angles are 120°). This orbital can be only half-occupied, which should lead to a distortion of the C–Au–C angles according to the Jahn–Teller theorem, removing the degeneracy thereby. T-shaped (XIV) or Y-shaped (XV) symmetry distortions are possible:

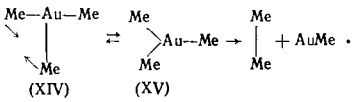


(XIV), $\alpha > 120^\circ$;

(XV), $\alpha < 120^\circ$.

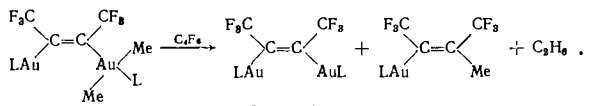
A molecular orbital calculation on the Me_3Au molecule has shown[64] that the T-shaped configuration (XIV) corresponds to the energy minimum. The vibrations of the two *cis*-Me groups towards one another lead to their spatial approach and a transition of the molecule to the Y-shaped configuration (XV), in which the coordination of the gold approaches

the linear form; under these conditions, elimination takes place:

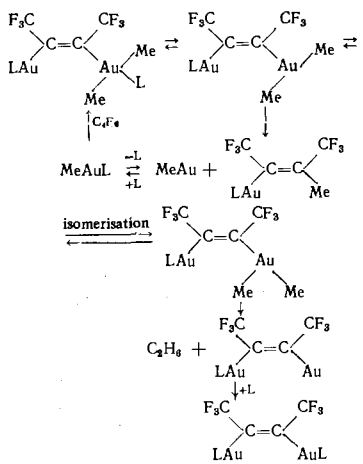


(XIV) (XV)

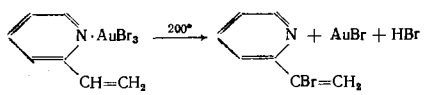
The only example of the elimination of an alkenyl group from a gold(III) complex is provided by the decomposition of the dinuclear hexafluorobutenyl derivatives (XI) catalysed by hexafluorobut-2-yne:[53]



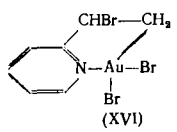
The mechanism proposed for this reaction is based on the hypothesis of the intramolecular *cis*-elimination:



A reductive elimination stage has been proposed for the thermolysis of the complex of $AuBr_3$ with 2-vinylpyridine[65]:



It has been suggested that gold adds initially to the C=C double bond with formation of the cyclic compound (XVI), from which AuBr and HBr are then split off:



(XVI)

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The data presented in the review show that the ability of a complex RAuL or the corresponding tervalent gold derivative to undergo oxidative addition or reductive elimination reaction depends greatly both on the group R and on the ligand L. However, it is at present difficult to reach an unambiguous conclusion concerning the nature of this dependence and particularly to give preference to steric or electronic factors.

The data on the oxidative addition of halogens and alkyl iodides to anionic complexes of univalent gold and to polyhalogenoaryl derivatives showed that these reactions involve in most cases *trans*-addition. However, the above conclusion cannot be extended to all types of organogold compounds, since, even within the framework of anionic complexes, there are deviations from the general rule for this class of compounds: the phenyl derivatives give rise to the *cis*-isomers. It is not clear whether this entials a change in the stereochemistry of the transition state or whether all aspects are determined by the difference between the thermodynamics of the *cis*- and *trans*-isomers of the compounds formed.

The oxidation-reduction interconversions of organometallic derivatives of univalent and tervalent gold have been little studied and, what is most important, only in isolated instances. In particular, reactions of organogold compounds with alkyl and especially aryl halides have been hardly investigated (the reaction of complexes of methylgold with methyl iodide is an exception). Despite this, one can already speak of the synthetic value of oxidative addition as a method of synthesis of organic derivatives of tervalent gold which are difficult to obtain.

Interesting results may be expected from the study of oxidative addition to zerovalent gold complexes, the first representative of which has been obtained quite recently[66].

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Polymeric Derivatives of Adamantane

A.P.Khardin and S.S.Radchenko

The literature data on the synthesis and properties of polymers with fragments of the polyhedral structures of adamantane and 1,1'-biadamantane are surveyed. The inter-relation between the structures of the polyhedral monomers and their reactivities is examined. A distinctive feature of the adamantane-containing polymers, together with their high thermal stability, is their resistance to hydrolysis and oxidation and to the action of light and solvents.
The bibliography includes 114 referenees.

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I. INTRODUCTION

Compounds with a polyhedral structure have attracted the attention of investigators from the standpoint of the possibility of obtaining polymers with valuable practical properties. An example of this is provided by the carbaborane-containing polymers the methods of synthesis of which are based on the functional transformations of carbaboranes—polyhedral systems with a boron–carbon skeleton[1].

One of the "growth points"[2] in organic chemistry at the present stage consists of studies in the field of polyhedral hydrocarbons and in the first place adamantane, first detected in petroleum by Landa[3] in 1933. These studies developed further after Schleyer et al.[4] achieved the isomerisation of tetrahydrobicyclopentadiene to adamantane in the presence of aluminium halide. The ease of this rearrangement can be accounted for by the high thermodynamic stability of adamantane; treatment of all the known $C_{10}H_{16}$ isomers with Lewis acid inevitably leads to this tricyclic hydrocarbon[5]. The antiviral activity of 1-aminoadamantane hydrochloride was discovered in 1964.[6] Since then there has been a continuous growth of the number of studies on adamantane and related polyhedral hydrocarbons; they have been surveyed in a whole series of reviews[7-19]. Certain special fields concerning heteroadamantanes[20,25] and the pharmacological activity of adamantane derivatives[21,22] have been examined. The first monograph on adamantane has been published recently[22].

Fairly numerous studies, described mainly in patents, have been made on polymeric adamantane derivatives. However, if one disregards a brief review on adamantane polymers[23] quoting four original communications, the literature on this field has not been surveyed. At the beginning of 1977 a review was published[24] on the structure and stereochemistry of adamantanoid hydrocarbons in which certain problems of the stereochemistry of polyadamantanes—low-molecular-weight linear polymers—were examined together with those concerning higher adamantane homologues. Studies on silicon-containing polymeric derivatives of adamantane have been described in a review[25].

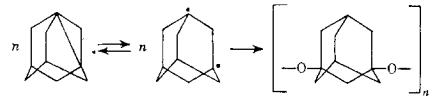
II. CARBOCHAIN POLYMERS OF ADAMANTANE

Polyadamantane was obtained for the first time[26] from 3,3'-dibromo-1,1'-biadamantane by the Wurtz reaction:



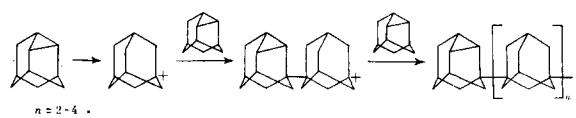
The polymer (melting point above 420 °C) was a white powder insoluble in the usual organic solvents and resistant to the action of concentrated hydrochloric acid and 5 *N* solution of alkali. According to X-ray diffraction data, the polyadamantane had a degree of crystallinity in excess of 80%.

Dehydroadamantanes may serve as another source of polyadamantane. 1,3-Dehydroadamantane is an extremely reactive compound; on heating to 130–160 °C, it is converted into a solid polymer without fusion[27]. In solutions in the presence of atmospheric oxygen 1,3-dehydroadamantane forms an adamantane polyperoxide with opening of the inner cyclopropyl ring even at room temperature[28]:



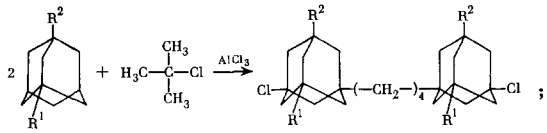
On heating, the polyperoxide decomposes explosively in the temperature range 146–180 °C.

Polyadamantane is also formed on polymerisation of 2,4-dehydroadamantane under the influence of aluminium chloride[29]. The reaction proceeds via a stage involving the formation of the adamantyl cation and subsequent hydride transfer from 2,4-dehydroadamantane:



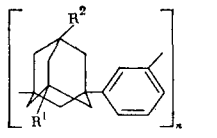
Interesting results have been obtained in the polycondensation of polybromoadamantanes under the influence of metallic sodium[30]. The product is a three-dimensional carbon polymer and consists of the carbon nuclei of adamantane. It consists of a white powder with a carbon content of ~ 99% and a density of 2 g cm^{-3}. It is insoluble in organic solvents.

Oligomers consisting of two and three adamantane nuclei and short methylene chains between them have been obtained by the polycondensation of adamantane and its homologues with alkyl halides in the presence of $AlCl_3$ or $AlBr_3$.[31] An example is provided by the reaction between alkyladamantane and t-butyl chloride:



R^1 and R^2 = CH_3, or C_2H_5

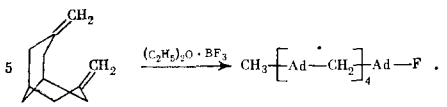
The process takes place at 20–30 °C in the course of 1 h. The number of nuclei in the chain can be increased by employing a large excess of the initial adamantane homologue. The copolymers of adamantane and benzene can serve as another example of mixed polyadamantanes[32]:



where R^1 and R^2 = alkyl and n = 9–10.

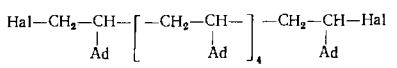
The reaction of alkyladamantane with di-t-alkylbenzenes takes place in the presence of Lewis acids at temperatures between 0° and +25 °C for equimolar reactant ratios. The resulting polymer with a molecular weight of 2300 is a solid, which melts at 250 °C and forms protective films and coatings with a high resistance to thermal oxidation[32].

Polyadamantane with methylene bridges in the chain is a product of the cationic polymerisation of 3,7-bismethylenebicyclo[3.3.1]nonane in an organic solvent (n = 4)[33]†:

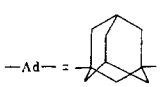


The polymer is insoluble in organic solvents and melts above 340 °C.

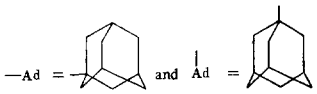
Certain polymers of vinyl derivatives of adamantane are known. Under the influence of $AlCl_3$ or $AlBr_3$ in methylene chloride, vinyladamantane gives rise to a solid product which is insoluble in organic solvents[34]. On the basis of the results of elemental analysis, a formula has been proposed for the oligomer#:



† Here and henceforth



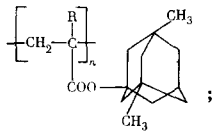
Here and henceforth



The homopolymer of 1-allyladamantane and its copolymer with vinylcyclohexane have been obtained by polymerisation in the presence of a complex catalyst—(iso-BuO)$_3$Al–$TiCl_4$.[35] However, no information about the properties of these polymers is presented in the relevant communication.

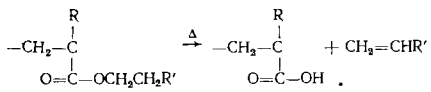
Adamantyl acrylates and methacrylates polymerise under the influence of free-radical and anionic catalysts[36,37] and also under ultraviolet irradiation[38].

The study of the kinetics of the radical polymerisation showed that both the methacrylates and the vinyl esters of adamantane derivatives are highly reactive[39], i.e. the adamantyl group does not inhibit polymerisation. The principal distinctive properties of such polymers are high glass points, considerable surface hardness, brittleness and low mechanical strength, and insignificant contraction on polymerisation. These properties are due to the presence in the macromolecules of the bulky adamantyl group, which increases the rigidity of the polymer chains:



R = H, or CH_3.

One of the causes of the thermal degradation of polyacrylates is the cleavage of the ester side-groups with formation of an olefin:

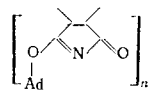


The reaction does not occur for poly(adamantyl acrylates) and this is a particular reason for their high thermal stability.

Solutions of poly(adamantyl acrylates) are very viscous, which led to their use as thickening agents for lubricating oils[38]. For example, a 1% solution of poly(dimethyladamantyl acrylate) with a molecular weight of 80000 has the same viscosity as a 2% solution of poly(methyl methacrylate) with a molecular weight of 117000.

Acrylate and methacrylate esters of adamantanols copolymerise with methyl methacrylate, styrene, acrylonitrile, and vinyl chloride[37]. The properties of the copolymers depend on their composition, but in all cases copolymerisation with adamantyl acrylates leads to an increase of the glass points and of the hardness of the copolymers.

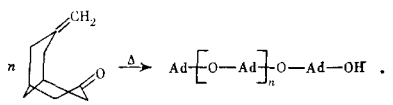
The influence of bulky substituents on the stereoregularity of the polymers of vinyl ethers and esters has been studied[42]. Investigation of the infrared spectra of the polymer films showed that the adamantyl group promotes a high syndiotacticity of the poly(vinyl carboxylate) and the isotacticity of the vinyl ether. The orienting effect of the adamantyl group is similar to that of the t-butyl group, which can be regarded as the open-chain analogue of the adamantyl group. Like adamantyl methacrylates, poly(adamantyl vinyl ethers) have high softening temperatures (210–225 °C). The homo- and co-polymerisation of the heterocyclic derivative 5-(1′-adamantyloxy)-2H, 2-pyrrolone with various vinyl monomers have been studied in detail[43]. Spectroscopic investigations have shown that the polymerisation takes place as a result of the partial dissociation of the C=C bond in the heterocycle:



The presence of the pyrrolone heterocycle in the polymer chain led the authors[43] to investigate the photochemical properties of the polymer films. It was found that, on ultraviolet irradiation, photochemical transformations, accompanied by the formation of cyclopropyl isocyanate groups, take place in the polymer. The copolymers of 5-(1′-adamantyloxy)-2*H*, 2-pyrrolone are characterised by an alternation of the comonomer units and the high values of the parameters $Q = 3.40$ and $e = 1.59$ indicate, according to the authors, electron-accepting properties of the substituent—the adamantyl group. The homo- and co-polymers of 5-(1′-adamantyloxy)-2*H*, 2-pyrrolone have high glass points (220–245 °C). On thermolysis of the homopolymer, the adamantyl group migrates to the nitrogen atom with formation of poly-*N*-(1-adamantyl)maleimide.

III. POLYETHERS, POLYESTERS, POLYSULPHONES, AND POLYCARBONATES OF ADAMANTANE

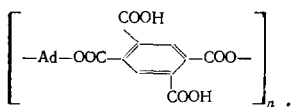
The polyether may have been the first polymeric heterochain derivative of adamantane obtained[44]. In their study of the possibility of synthesising the adamantane nucleus from bicyclic systems, Stetter et al.[44] observed that, when 3-methylenebicyclo[3.3.1]-7-nonanone is heated in an inert solvent in the presence of toluene-*p*-sulphonic acid, a polyether derived from adamantane is formed with a quantitative yield:



Polyethers have been synthesised by the reaction of the phenoxides derived from 1,3- and 2,2-bis(4′-hydroxyphenyl)-adamantanes with di(4-chlorophenyl) sulphone and 4,4′-difluorobenzophenone[45] and also by the reaction of 3,3′-dibromo-1,1′-biadamantane with diphenoxyethane[40,41].

Numerous studies, described mainly in patents[46–55], have been devoted to the synthesis of polyesters based on adamantanedicarboxylic acids or adamantane diols. The starting compounds for the synthesis of adamantane-containing polyesters are either the diesters of adamantanedicarboxylic acids (transesterification with glycols) or the highly reactive chlorides of the corresponding dicarboxylic acids. Calcium acetate–antimony dioxide[40] and sodium hydride–hexabutoxytitanate[41] systems as well as tetraisopropyl titanate and toluene-*p*-sulphonic acid[46–48] can be used as transesterification catalysts. The chloride of adamantane-1,3-dicarboxylic acid is highly reactive. The rate constant for its reaction with diethylene glycol, for example, in the temperature range 100–140 °C varies from 0.0044 to 0.0203 litre mol^{-1} s^{-1}.[56]

The majority of the polyesters have a low molecular weight owing to the steric influence of the adamantane nucleus. This is demonstrated by the esterification of adamantane-1,3-diols by tetracarboxylic acid dianhydrides[51]. If the reaction is carried out in dimethylformamide (DMF) at a low temperature (60 °C) and in the presence of toluene-*p*-sulphonic acid, then a linear non-cross-linked polyester with free carboxy-groups is obtained:



This can be explained by the fact that, in the esterification of the first carbonyl group in one of the anhydride moieties by adamantane-1,3-diol, the bulky adamantyl group causes steric hindrance of the reaction of the second adamantanediol molecule with the carbonyl group adjoining the esterified group. On the other hand, the second anhydride moiety is not sterically hindered and reacts with the diol. This type of polyester is soluble in 5% aqueous sodium bicarbonate solution and can be cross-linked by glycols, di-isocyanates, and other functional compounds and also on heating. Some of the properties of the linear polyesters are presented in Table 1.

Table 1. The properties of adamantane-containing polyesters.

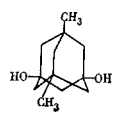
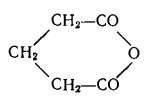
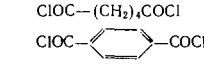
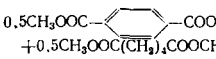
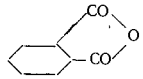
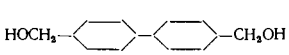
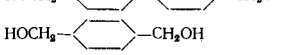
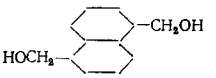
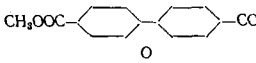
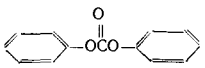
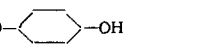
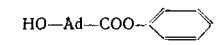
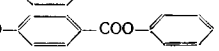
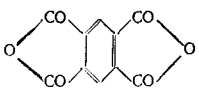
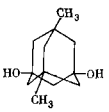
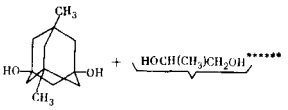
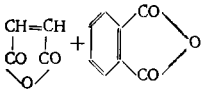
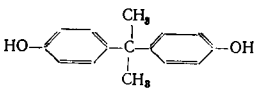
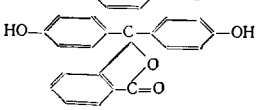
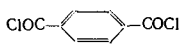
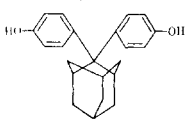
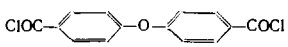
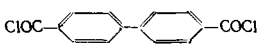
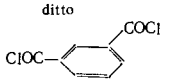
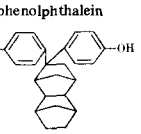
Dicarboxylic acid or its derivative	Diol	(MW)*	t_s^{**}, °C	Characteristics of polymer****	References
$C_2H_5OOCCH_2COOC_2H_5$		0.9 (1616)	99***	solid, brittle	[46, 47, 55]
	ditto	0.25 (4430)	51***	solid, vitreous	[46, 47, 55]
$ClOC-(CH_2)_4COCl$	»	0.08 (925)	12***	viscous liquid	[46, 47, 55]
	»	0.09 (1490)	165***	30% crystallinity	[46, 47, 55]
	»	0.11	160***	—	[46, 47, 55]
	»	0.32	110***	solid, vitreous	[55]
$CH_3OOC-Ad-COOCH_3$	$HO(CH_2)_2OH$	—	—	viscous liquid	[40, 41]
$CH_3OOC-Ad-COOCH_3$	$HOCH_2-Ad-CH_2OH$	0.23	—	*stable on heating* to 325 °C	[40, 41]
ditto		0.25	230	resistant to u.v. light	[40, 41]
»		0.48	170	—	[40, 41]

Table 1 (cont.)

Dicarboxylic acid or its derivative	Diol	η_{ln} (MW)*	t_s^*, °C	Characteristics of polymer****	References
$CH_3OOC-Ad-COOCH_3$	$HOCH_2-C_6H_4-CH_2OH$	0,37	250	—	[40, 41]
»		0,20	140	—	[40, 41]
	$HOCH_2-Ad-CH_2OH$	0,30	210	—	[40, 41]
	ditto	0,20	260	—	[40, 41]
ClOC—Ad—COCl		1,0	194—200	stable on heating to 350 °C	[49]
		(17500)	310	—	[50]
$CH_3OOC-Ad-COOCH_3$	$HO(CH_2)_4OH$	—	138***	stable on heating to 350 °C	[52]
		—	—	solid powder soluble in 5% aqueous NaOH	[52]
		—	—	d=1,16; σ_f=32,6	[48]
	ditto ******	—	—	τ_0=305° C; d=1,17; σ_b=67.7	[48]
ClOC—Ad—COCl		0.57*****	300	τ_0=360° C	[53]
ClOC—Ad—COCl	$HOCH_2-C_6H_4-CH_2OH$	0,45****	230	—	[53]
ditto		0.75****	315	τ_0=350° C	[53]
»	$HO(CH_2)_4OH$	0.33*****	90	—	[57]
		0.51	—	τ_0=420° C, crystalline	[58]
ditto	ditto + bisphenol A	0.82	280	τ_0' = 330 °C, soluble in chloroform, DCE, TCE, and tricresol	[59]
»	ditto + phenolphthalein	0.85	330	τ_0' = 330 °C, soluble in chloroform	[59]
	ditto + bisphenol A	0.90	265	τ_0=340° C, ditto	[59]
ditto	ditto + phenolphthalein	0,58	290	τ_0=340° C, ditto	[59]
	ditto + bisphenol A	0.36	285	τ_0 = 330 °C, soluble in TCE + tricresol mixture	[59]
ditto	ditto + phenolphthalein	0.15	310	τ_0=360° C, ditto	[59]
	ditto + bisphenol A	0.27	260	τ_0=320° C, ditto	[59]
ditto	ditto + phenolphthalein	0,14	300	τ_0=340° C, ditto	[59]
»	ditto + 	0.30	290	τ_0=340° C, soluble in TCE	[59]

* Logarithmic viscosity η_{ln} measured in a phenol (60%)–tetrachloroethane (40%) mixture; the molecular weight (MW) was measured osmometrically in benzene.

** Softening temperature.

*** Reduced glass point (according to thermogravimetric data).

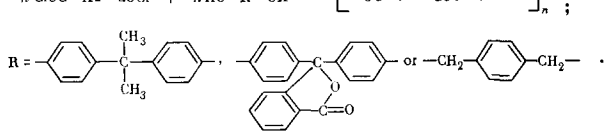
**** Notation: τ_0 = temperature of onset of weight loss; d = density (g cm^{-3}); σ_f = flexural strength (MPa).

***** The intrinsic viscosity η_{int} is given.

****** Hardened with styrene.

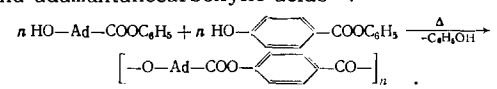
Unsaturated polyesters, which subsequently acquire a structure in the presence of peroxides, can be obtained by the reaction of adamantane-1,3-diol with maleic anhydride. Their composition and properties can be varied within wide limits by adding other dianhydrides, for example, phthalic dianhydride or comonomers—styrene and methyl methacrylate[48].

The polyesterification of the chloride of adamantane-1,3-carboxylic acid by bisphenols in high-boiling solvents[53] or under the conditions of acceptor-catalytic polycondensation in solution[54] leads to adamantane-containing polyesters with a fairly high molecular weight:



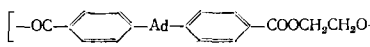
Mixed polyarylates have been synthesised by the high-temperature polycondensation of 2,2-bis(4′-hydroxyphenyl)-adamantane, cardo-bisphenols, and the chlorides of isophthalic and terephthalic acids[58,59]. The polyarylates have a crystalline structure and the degree of their crystallinity depends on the content of adamantane groups.

Mixed polyesters have also been obtained by the joint polyesterification of the phenyl esters of aromatic hydroxy-acids and adamantanecarboxylic acids[50]:



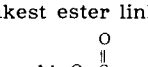
The reaction is carried out under fairly severe conditions (330 °C, 0.3 mmHg) in the presence of dibutyltin as the catalyst.

Thermostable adamantane-containing polyesters, produced by the bulk condensation of 1,3-bis(4′-methoxycarbonylphenyl)adamantane with ethylene glycol, have been described[52]:

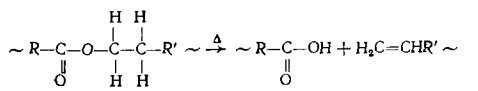


The reaction is carried out under conditions resembling those in the synthesis of poly(ethylene terephthalate). In the first stage at 160 °C and 0.3 mmHg a diglycol ether is obtained and is then gradually heated in the presence of antimony oxide to 245 °C at a pressure of 0.15 mmHg.

Adamantane-containing polyesters have fairly high glass points and softening temperatures (Table 1) and it has been noted in a number of studies[46,47,55] that they are highly resistant to thermal and oxidative degradation and exhibit an effective hydrolytic stability. This is particularly notable when adamantanediol is used. In this case the adamantane nucleus adjoins the weakest ester linkage

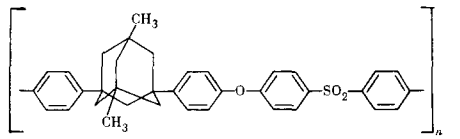


and prevents its being acted upon by hydrolysing agents[46]. In addition one of the ways of decomposing the polyesters involves the elimination of hydrogen from the β-position in the alcoholic residue with formation of two fragments of the macromolecule with terminal carboxy- and olefinic groups:

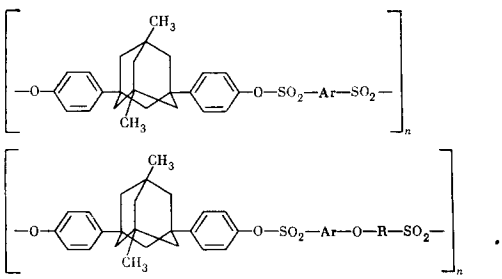


On the other hand, the formation of a double bond in the adamantane nucleus is impossible under these conditions, so that the decomposition of adamantanediol polyesters is difficult[55]. Both linear and cross-linked polyesters are highly resistant to the action of ultraviolet light and sunlight[48]. These properties make adamantane-containing polyesters useful as protective coatings and packing materials.

A whole series of polyesters based on 1,3-bis(4′-hydroxyphenyl)-5,7-dimethyladamantane have been described. The reaction of the latter with di(halogenophenyl) sulphones yielded polysulphones, for example[60]:



The reaction is carried out in an organic solvent in air at 160 °C. A necessary condition is preliminary synthesis of the disodium salt of a bisphenol by the reaction of the latter with an aqueous NaOH solution. Using bisarenesulphonic acid esters or chlorides instead of dihalogenosulphones, one can obtain the corresponding polysulphonates[61,62]:



Triethylamine is used as the HCl acceptor. The reaction takes place fairly rapidly (1—2 h) and yields a high-molecular-weight product with an intrinsic viscosity of 1.1—1.2 dl g^{-1}. In contrast to the usual polysulphonates, the adamantane-containing polysulphones and polysulphonates are rigid and strong but not brittle. They soften at 180 °C and exhibit a high resistance to oxidation.

Table 2. The properties of polycarbonates and copolycarbonates based on 1,3-bis(4′-hydroxyphenyl)adamantane and bisphenol A.[63,64]

Property	Bisphenol A	1,3-bis(4′-hydroxyphenyl)adamantane	Bisphenol A: 1,3-bis(4′-hydroxyphenyl) adamantane = 1 : 1
Glass point, °C (DTA)	150	225—250	211—212
M.p., °C	220—230	stable up to 300	—
τ_0, °C	—	285	250
η_{in} (in methylene chloride)	0.59	0.69	0.76
n_D^{20}	1.585	1.578—1.582	1.582—1.586
Shore hardness	80±2	83±2	80±1
σ_t, MPa	85.5	58	91
ϵ_{rel}, %	80	8	19
E_t, MPa	1650	868	800
Density, g cm^{-3}	1.199	1.148	1.167

Bisphenols derived from adamantane have been used in the synthesis of polycarbonates and copolycarbonates. 1,3-Bis-(4′-hydroxyphenyl)adamantane is treated with phosgene in solution in methylene chloride in the presence of pyridine at 25—30 °C.[63] The copolycarbonate derived from 1,3-bis(4′-hydroxyphenyl)adamantane and 2,2-bis(4′-hydroxyphenyl)-propane (bisphenol A), taken in equimolar proportions, is obtained under analogous conditions[64]. Table 2 presents

certain properties of adamantane-containing co- and polycarbonates and compares them with a commercial polycarbonate—Lexan.

Bisphenols containing the adamantane nucleus in the form of a cardo-group have also been proposed for the synthesis of polycarbonates[65]. Depending on the method of preparation (low-temperature or interfacial polycondensation), these polycarbonates have crystalline or amorphous structures. The presence of adamantyl cardo-groups in the polycarbonates leads to an appreciable increase of their heat resistance and thermal stability. Depending on the structure of the bisphenol, the softening temperature is 240–310 °C and the temperature of the onset of decomposition is 300–350 °C.

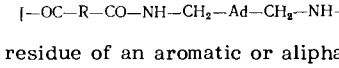
IV. ADAMANTANE-CONTAINING POLYAMIDES

Polyamides are some of the first polymers for which the effectiveness of the introduction of adamantane nuclei into polymer chains has been demonstrated. Adamantane-containing polyamides, obtained in the melt, like nylon-6,6, from a salt of 1,3-diaminoadamantane and sebacic acid[66] or a salt of adamantanedicarboxylic acid and 1,4-bis(aminomethyl)-cyclohexane[67], have a low molecular weight.

The conditions for the synthesis of the polyamides from the chloride of adamantane-1,3-dicarboxylic acid by emulsion and interfacial polycondensation have been studied in detail[67–69].

In the first case a high-molecular-weight polyamide (η_{ln} = 1.45) can be obtained in a high yield by carrying out the process in the presence of a small excess of the acid chloride at 10–30 °C and for an overall concentration of the reactants of 0.33 M. The reaction is performed by pouring a solution of the acid chloride in tetrahydrofuran (THF) into an aqueous solution of the diamine. Sodium carbonate is used as the HCl acceptor. In the interfacial polycondensation a solution of the acid chloride in an aromatic or chlorinated hydrocarbon is added with stirring to an aqueous solution of the diamine. Pyridine, triethylamine, and NaOH can also serve as the HCl acceptors.

High-molecular-weight polyamides with $\eta_{ln} \leq 5.0$ and having the general formula[70]



where R is a residue of an aromatic or aliphatic dicarboxylic acid, have been obtained by the solid-phase polycondensation of a salt of a mixed diamine—1,3-bis(aminomethyl)adamantane—with a dicarboxylic acid. The properties of the polyamides obtained are presented in Table 3.

Among adamantane-containing polyamides, poly(*m*-phenyleneadamantylene-1,3-dicarboxamide)—the product of the condensation of *m*-phenylenediamine with the chloride of adamantane-1,3-dicarboxylic acid—is of greatest interest:

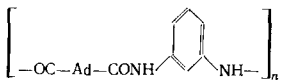
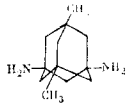
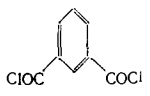
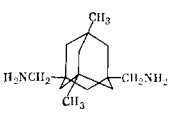
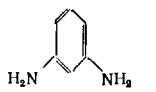
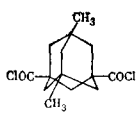
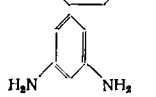


Table 3. The properties of adamantane-containing polyamides.

Dicarboxylic acid or its chloride	Diamine	η_{ln}^{+}	M.p., °C	Characteristics of polymer**	References
$HOOC(CH_2)_6COOH$ ClOC—Ad—COCl	H_2N—Ad—NH_2 H_2N—Ad—NH_2	— 0.11	153 —	— —	[66] [66]
ClOC—Ad—COCl		0.12	320	—	[67]
		0.82	240	transparent, vitreous	[70]
ClOC—Ad—COCl ditto	$H_2N(CH_2)_6NH_2$ ditto	1.14 1.79	316 197	— d = 1.16; σ_t = 50; ϵ_e = 3; σ_f = 327.5; water absorption = 0.34%	[69] [69]
ClOC—Ad—COCl		1.45	294	d = 1.256; σ_t = 117; E_t = 586; ϵ_e = 13; water absorption = 1.52%	[49, 69]
	$H_2N(CH_2)_6NH_2$	1.46***	210***	σ_f = 110; E_f = 4280	[49, 67]
ditto	H_2NCH_2——CH_2NH_2	0.21	—	brittle	[67]
»		0.75	320	σ_t = 65.5; ϵ_e = 16	[49, 67]

* For polyamides Nos. 5–7, in concentrated sulphuric acid; for the remaining polymers, in *m*-cresol.

** Notation: E_t = tensile modulus (MPa); for the remaining notation, see the footnotes to Tables 1 and 4.

*** Molecular weight (3–4) × 10^4.

**** Glass point 145 °C.

Films and fibres can be obtained from it by appropriate methods. The properties of a polyamide film of this kind are presented in Table 4.[49] The polyamide softens at 294 °C and loses not more than 0.86% of its weight on being kept in air for 2 h at 325 °C.

Table 4. Properties of a poly-*m*-phenyleneadamantane-1,3-dicarboxamide film[49].

Property*	20° C	150° C	250° C
σ_f	153.8	—	—
E_f	4178	—	—
σ_t	117.2	75.8	34.5
ϵ_e	13	11	6
H_R	112	—	—

* Notation: σ_f = flexural strength (MPa); E_f = flexural modulus (MPa); σ_t = tensile strength (MPa); ε_e = elongation at break (%); H_R = Rockwell hardness.

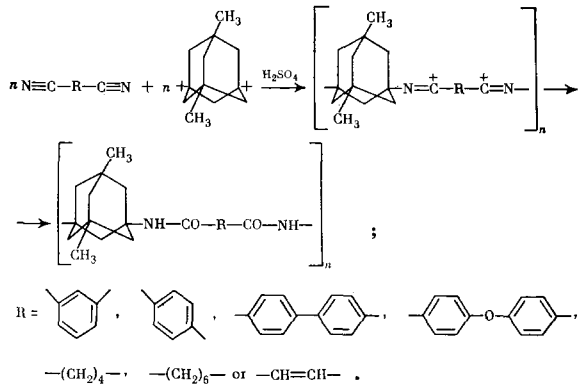
A fibre can be obtained from a solution of this polyamide in DMF by the wet moulding method[71]. An interesting feature of poly(*m*-phenyleneadamantylene-1,3-dicarboxamide) is that both the polyamide itself and the fibre obtained from it are amorphous and, in contrast to many polymers, the fibre does not crystallise on being kept at temperatures in the range between the glass and yield points. A special technique was therefore developed for drawing the moulded fibre in contact with a hot plate which makes it possible to follow the morphological changes occurring in the fibre during such treatment over a narrow temperature range[72]. The fibre has been drawn at 325 °C with a drawing factor of 6:1 and at a drawing rate of 220000% min^{-1}. The properties of the drawn fibre are presented in Table 5.[73]

Table 5. The properties of fibre based on poly-*m*-phenyleneadamantylene-1,3-dicarboxamide.

Property	Fibre	
	moulded	drawn
[η] (conc. sulphuric acid)	1.5	—
Linear density (denier)	—	7.3
Strength, g $denier^{-1}$	0.62	4.0
Initial modulus, g $denier^{-1}$		51.4
ϵ_e, %	19.9	—
Elasticity, %	72.2	25.2

However, in this case too the crystallinity of the fibre is low. The fibre is crystallised when it is kept in DMF or dimethylacetamide vapour. The fibre which was extended beforehand crystallises under these conditions in the course of several seconds[74]. The polyamide fibre has a high thermal stability, retaining 50% of its initial strength on being kept at 250 °C for 100 h[71].

A method employing the ability of dihalogeno- or dihydroxyadamantanes to form carbonium ions in highly ionising medias such as concentrated sulphuric or polyphosphoric acid has also been proposed for the synthesis of adamantane-containing polyamides[75,76]. The second reagent is an aliphatic, aromatic, or alicyclic dinitrile. The concentration of sulphuric acid is of decisive importance in this reaction; if it is below 99%, then the rate of polymerisation is low and the oxidative decomposition of the reactants predominates. At an acid concentration above 118% the process becomes difficult to control and is accompanied by the decomposition of the polyamide formed. The mechanism of this reaction can be illustrated by the following scheme:



In sulphuric acid, the reaction is carried out in the temperature range between −10° and 20 °C and in polyphosphoric acid between 70° and 110 °C. Polyamides have been obtained by this method in almost quantitative yields with η_{ln} between 0.5 and 1.2 and glass points in excess of 300 °C.

V. ADAMANTANE-CONTAINING POLYURETHANES

Adamantane-containing polyurethanes can be obtained by the reaction of 1,3-adamantylene di-isocyanate[77] or 1,3-di-isocyanato-5,7-dimethyladamantane[78] with polyols, which are usually polyalkylene or polyoxyalkylene glycols, polyester glycols, castor oil, and sorbitol polyesters. The reactivity of adamantylene di-isocyanate is considerably lower than that of aromatic di-isocyanates (Table 6). In the synthesis of adamantane-containing oligoester-urethanes it is therefore necessary to employ catalysts—NEt_3 or dibutyltindilaurate[80].

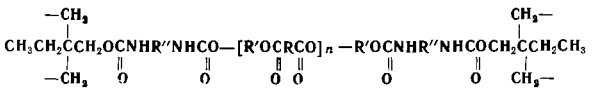
Table 6. The constants for the interaction* of di-isocyanates with poly(diethylene glycol adipate)[79].

Di-isocyanate	10^2k, litre mol^{-1} s^{-1}
2,4-Tolylene di-isocyanate	31.30
1,6-Hexamethylene di-isocyanate	5.26
1,3-Bis(isocyanatomethyl)adamantane	3.27
1,3-Adamantylene di-isocyanate	0.59

* k = reaction rate constant.

The hardening of liquid urethane rubbers with 1,1,1-tris-(hydroxymethyl)propane is fairly slow and the formation of a three-dimensional polyurethane network at 80 °C terminates after 10–12 h.[81] The properties of vulcanised polyurethanes are presented in Table 7. The increase in the chain lengths of oligomeric polyesterurethanes, based on tetramethylene glycol, when they interact with diamines[66] or with hydrazine hydrate[82] leads to the formation of light-resistant adamantane-containing polyurethane-ureas from which "Spandex" fibre is made. The films obtained from solutions of this polymer in DMF are transparent and have a low optical density and a high resistance to ultraviolet light (Table 8).

Table 7. The properties of adamantane-containing network polyurethanes* [81]



R	R′	R″	M_{av} (calc.)	10^3[Ad], mol g^{-1}	σ_t	ε_e, %	ε_0, %	TM2 hardness, rel. units	M.p., °C	$t_{o.d.}$
—$(CH_2)_4$—	—$(CH_2)_2$—O—$(CH_2)_2$—	—$(CH_2)_6$—	1280	0	9.3	450	1.5	0.56	—25÷—31	—
—$(CH_2)_4$—	ditto	—Ar—	1230	0	33.3	240	2.0	0.76	—15÷—22	270
—$(CH_2)_4$—	»	—Ad—	1420	1.41	37.1	225	1.5	0,80	20÷80	265
—$(CH_2)_4$—	»	—CH_2AdCH_2—	1480	1.35	23.5	380	2.5	0.60	2÷5	230
—Ad—	»	—$(CH_2)_6$—	1050	1.72	32.9	320	2.0	0,67	0÷8	240
—Ad—	»	—Ar—	1060	1.75	42.1	120	2.0	0.90	70÷74	270
—Ad—	»	—Ad—	1170	3.25	41.2	140	2.2	0.91	60÷66	270
—Ad—	—$(CH_2)_2O(CH_2)_2O(CH_2)_2$—	—$(CH_2)_6$—	1080	1.48	34.1	350	1.5	0.60	—10÷—16	—
—Ad—	ditto	—Ar—	1000	1.47	37,2	180	2.0	0.88	30÷36	—
—Ad—	»	—Ad—	1200	3.00	39.7	220	1.5	0.88	25÷30	250
Polyoxypropylene glycol		—Ad—	1550	1.29	17.2	478	2.5	1.00	—22÷30	220
—Ad—	—$(CH_2)_2$—O—$(CH_2)_2$—	—CH_2AdCH_2—	1230	3.12	24.5	285	3.0	0.73	38÷45	—

* Notation: Ar =  ; ε_0 = residual deformation at break; M_{av} = average molecular weight of the network polymer; $t_{o.d.}$ = temperature of onset of decomposition; for the significance of the remaining parameters, see the footnotes to Tables 1 and 4.

Table 8. Changes in the properties of linear polyurethanes on irradiation with ultraviolet light (in a AIPST-2-4-2 optical weather apparatus)[83]*.

Di-isocyanate	Before irradiation			After irradiation		
	σ_t	ϵ_e	D	σ_t	ϵ_e	D
1,3-Adamantylene di-isocyanate	3.3	187	0.1	2.2	122	0.14
Diphenylmethylene di-isocyanate	3.7	123	0,41	2.3	50	1.16
1,3-Bis(isocyanatomethyl) adamantane	3.1	346	0.1	2.2	245	0 14

* Notation: D = optical density (relative units); for the significance of the remaining notation, see the footnote to Table 4.

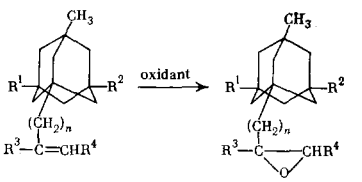
The replacement of 1,3-adamantylene di-isocyanate by 1,3-bis(isocyanatomethyl)adamantane makes it possible to obtain light-resistant polyurethanes with a higher elasticity[84]. An increase of light resistance is observed also for cross-linked polyurethanes. Thus polyurethane films obtained from poly(diethylene glycol adipate), 1,3-adamantylene di-isocyanate, and 1,1,1-tris(hydroxymethyl)propane turn yellow to a much lesser extent and lose 33% of the initial strength on irradiation with ultraviolet light, compared with films based on 2,4-tolylene di-isocyanate (72% loss of strength).[85] The rate of gas evolution from adamantane-containing polyurethanes under these conditions is lower by a factor of two, while the rate of absorption of oxygen is lower by a factor of 1.5 than for polyurethanes based on 1,6-hexamethylene di-isocyanate and 2,4-tolylene di-isocyanate.

Another advantage of adamantane-containing polyurethanes is their increased hydrolytic stability. This effect is particularly notable when the adamantylene group is attached to an ester group, i.e. for polyurethanes obtained from adamantane-containing oligoester-glycols[85]. The films obtained from such a polyurethane do not change in the course of three months in 5% H_2SO_4 and NaOH solutions and swell only by 3%, while similar polyurethanes derived from aliphatic oligoester-glycols decompose after 20–25 days.

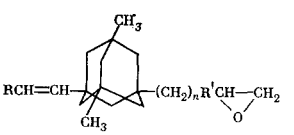
The products of the interaction of 1,3-adamantylene di-isocyanate with 1,3-diaminocyclohexane or 1,4-diaminobutane as well as butane-1,4-diol have been described[66]. In the first case the products are polyureas soluble in DMF and melting at 275 °C and in the second the product is a thermoplastic film-forming polyurethane.

VI. EPOXY-RESINS BASED ON ADAMANTANE DERIVATIVES

Adamantane-containing epoxides have been obtained by the oxidation of the corresponding alkenyladamantanes[86,87]:



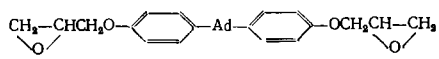
The oxidants are organic and inorganic peroxides, hydroperoxides, and hydrogen peroxide. The oxidation is carried out in the liquid phase in the temperature range from 5° to 50 °C in the presence of $Mo(CO)_6$. Epoxyadamantanes are obtained in yields up to 86% and are purified by distillation. Vinyl- and allyl-epoxyadamantanes having the general formula



can be obtained in this way. Polymerisation of these compounds in the presence of tri-isobutylaluminium and aluminium trisacetylacetonate yielded polyepoxides which are viscous liquids or solids and are likely to be useful as additives to lubricating oils and as components of adhesives. Polyepoxides with vinyl or allyl groups can be vulcanised, giving rise to rubber-like materials[86].

The reaction of adamantane-1,3-diol with the anhydride of cyclohexenecarboxylic acid led to the formation of a diester, which was converted into the bis-3,4-epoxycyclohexanecarboxylic acid ester of adamantane-1,3-diol by epoxidation with peracetic acid[88]. The product has a melting point of 31–32 °C and contains 19.8% of epoxy-groups.

The bisphenol derived from 5,7 dimethyladamantane[89], which reacts with epichlorohydrin in the presence of NaOH at 85–100 °C, is used as the starting compound for the synthesis of epoxy-resins. After isolation and washing free of salts, by the usual methods, the epoxy-resin

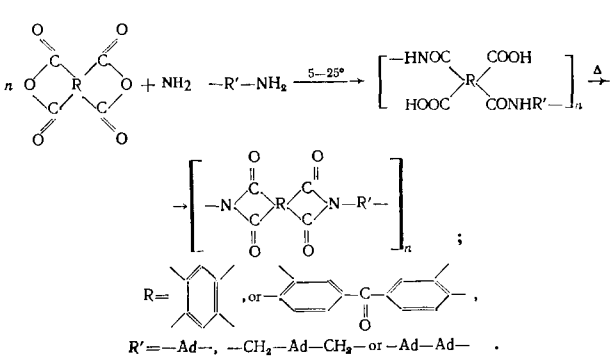


is a solid glass-like product of amber colour which melts at 47 °C.

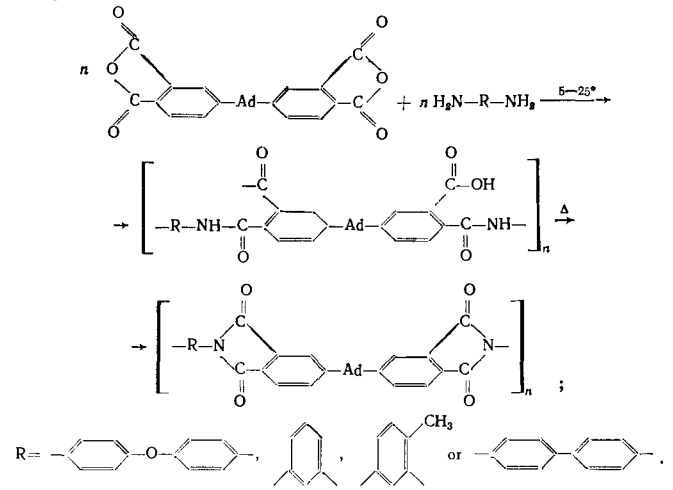
The hardening of epoxy-resins based on the bisphenols derived from adamantane, 1,1'-biadamantane, and isopropylidene on heating has been investigated[90,91]. The degree of hardening was inferred from the disappearance of the 415 cm^{-1} absorption band (due to the epoxy-group) in the infrared spectra and from determinations of the hardness of the specimens. Complete hardening was achieved after 13 h at 165 °C for the diglycidyl ether of the isopropylidenebisphenol, after 20 h at 200 °C for the diglycidyl ether of the bisphenol from adamantane, and after 88 h at 250 °C from the diglycidyl ether of the bisphenol from 1,1'-biadamantane. The hardened epoxy-resins derived from adamantane and 1,1'-biadamantane are superior as regards heat resistance and thermal stability to the polyepoxide with the isopropylidene groups. The softening temperatures of these resins are 250° and 220 °C compared with 180 °C for the polyepoxide based on the isopropylidenebisphenol, while the temperature of the onset of weight loss is 390° against 340 °C. In addition, they decompose at 400 °C leaving a larger amount of carbon residue than the corresponding polyepoxides without adamantane rings.

VII. CYCLOCHAIN POLYMERS OF ADAMANTANE

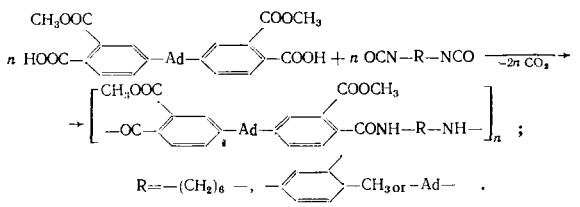
Among the cyclochain polymers with adamantane fragments in the main chain, polyimides have been most thoroughly investigated. They have been synthesised by a two-stage scheme. In the first stage a polyamidoacid is obtained by the reaction of diaminoadamantane with the dianhydride of an aromatic tetracarboxylic acid[92,93]:



The polyamidoacid is an intermediate in the reaction between an aromatic diamine and 1,3-bis(3',4'-dicarboxyphenyl)adamantane[94,95]:



In the second stage the polyamidoacid is subjected to cyclodehydration by heating it *in vacuo* at temperatures up to 300 °C. The reaction between the adamantane-containing dianhydride and the adamantane-containing diamine leads to low-molecular-weight polyamidoacids which are insoluble in organic solvents[92,96]. A similar result has been noted also in the synthesis of polyamidoesters by the reaction of the dimethyl ester of 1,3-bis(3',4'-dicarboxyphenyl)adamantane with di-isocyanate[97]:



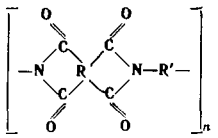
The basicity of adamantane-containing diamines is fairly high (pK_{a1} = 16.22–17.75) and that of 1,3-bis(aminoethyl)adamantane is at the level of aliphatic amines[98]. The formation of low-molecular-weight polyamidoacids is more likely to be explained by the low solubility and the reduced reactivity of the adamantane-containing dianhydride[99].

High-molecular-weight soluble adamantane-containing polyamidoacids with an intrinsic viscosity up to 4.8 dl g^{-1} are obtained when the above reactions are carried out in an aprotic solvent—inorganic salt system[100]. For example, in the presence of LiCl the rate constants for the formation of adamantane-containing polyamidoacids increase by a factor of 5–5.5.[99]

A distinctive feature of adamantane-containing polyimides is their high resistance to hydrolysis and the action of organic solvents and certain chemicals. A film made of the polyimide based on 1,3-bis(3',4'-dicarboxyphenyl)adamantane and di(4-aminophenyl)ether loses not more than 14% of its initial strength after a five day exposure to a 10% solution of NaOH and does not dissolve in concentrated H_2SO_4; on the other hand, the polyimide film based on pyromellitic dianhydride decomposes under analogous conditions[95].

A similar effect is also achieved when 1,3-bis(aminoethyl)-adamantane is used[101]. The introduction of 20% of this diamine instead of di(4-aminophenyl)ether in the synthesis of a polyimide based on pyromellitic dianhydride increases by a factor greater than 2 the hydrolytic stability of the polyimide film.

Table 9. The properties of adamantane-containing polyimides.



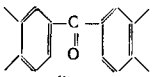
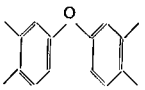
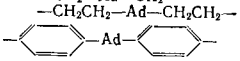
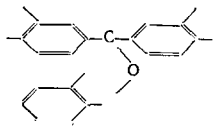
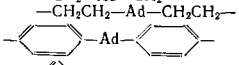
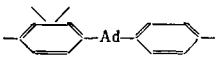
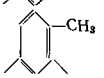
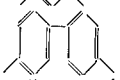
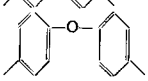
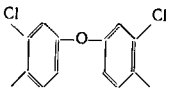
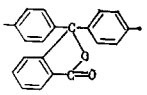
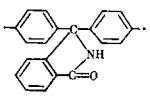
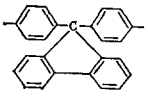
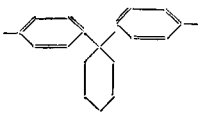
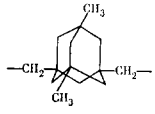
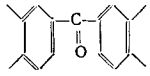
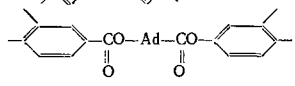
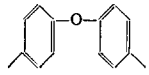
R	R'	η_{int}* (PAA)	M.p., °C	$t_{o.d.}$, °C	Characteristics of polymer**	References
	—Ad—	—	310	400	—	[93. 103]
ditto	—CH_2—Ad—CH_2—	—	210	390	—	[93. 103]
»	—Ad—Ad—	—	—	330	—	[93]
	—Ad—	—	240	380	—	[93. 103]
ditto	—CH_2—Ad—CH_2—	—	200	340	σ_t = 131.3	[93, 103]
»	—Ad—Ad—	—	—	330	—	[93]
	—Ad—	0.10	230	360	crystalline	[104. 108]
ditto	—CH_2—Ad—CH_2—	0.87	215	450	amorphous	[104, 108]
»	—CH_2CH_2—Ad—CH_2CH_2—	0.44	165	410	ditto	[104. 108]
»		0.78	305	440	»	[104 108]
	—Ad—	0.26	290	430	»	[104. 108]
ditto	—CH_2—Ad—CH_2—	0.83	260	425	amorphous	[104, 108]
»	—CH_2CH_2—Ad—CH_2CH_2—	0.34	215	415	ditto	[104, 108]
»		0.89	350	430	»	[104, 108]
		1.72	—	380	σ_t = 105.8; ϵ_e = 5–7; d = 1.48	[94, 95, 100]
ditto		4.80	—	—	—	[100]
»		1.59	—	380	σ_t = 90.2; ϵ_e = 3–6; d = 1.42	[94, 95, 100]
»		3.30	—	380	σ_t = 112.7; ϵ_e = 5–8; d = 1.44	[94, 95, 100]
»		2.20	—	345	σ_t = 106.8; ϵ_e = 5–7; d = 1.46	[94, 95, 100]
»		0.19	—	—	—	[100]
»		1.02	—	420	—	[102]
»		0.96	—	415	—	[102]
ditto		1 26	—	425	—	[102]
»		0.68	—	410	—	[102]

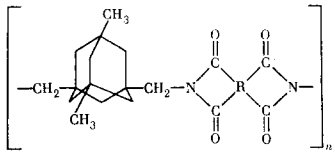
Table 9 (cont.)

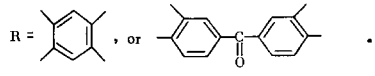
R	R′	η_{int}* (PAA)	$t_{o.d.}$, °C	M.p., °C	Characteristics of polymer**	References
		—	—	370	—	[105, 106]
	ditto	—	—	370	—	[105, 106]
		—	235	390	—	[107]

* In *N*-methyl-2-pyrrolidinone at 25 °C; PAA = polyamidoacid.
** For the designations and dimensions of the parameters, see the footnotes to Tables 1 and 4.

A whole series of soluble adamantane-containing polyimides with a high resistance to hydrolysis and an increased resistance to thermal oxidation have been obtained from cardo-diamines and cardo-dianhydrides[102-104]. They were synthesised in a single stage by heating the reactants in nitrobenzene to 210 °C. The polyimides soften on heating and can be worked by pressing or by casting from solution.

The polyimides obtained from the dianhydrides of aromatic tetracarboxylic acids and 1,3-bis(aminomethyl)-5,7-dimethyladamantane have an interesting property[105,106]:

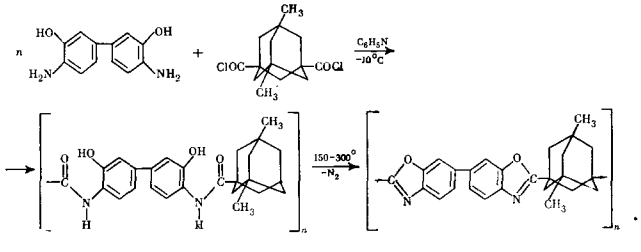




While their thermal stability is not inferior to that of aromatic polyimides, they are colourless—in contrast to the former polymers they do not have a characteristic yellow colour. Compared with similar polyimides based on 1,3-diaminoadamantane, they have a higher molecular weight. The properties of the polyimides synthesised are presented in Table 9.

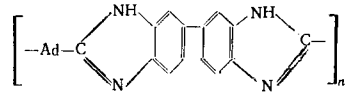
Heat-resistant polyester imides are obtained by the reaction of aromatic diamines with 1,3-adamantylenebistrimellitic dianhydride[107]. The polyimidoacid obtained in the first stage (viscosity 5.5 S) is converted into the imido-form at 300 °C for 16 h. The resulting polyester-imide film does not decompose on heating to 390 °C and has a glass point of 235 °C.

Adamantane-containing polybenzoxazoles obtained by low-temperature polycondensation from the chloride of 5,7-dimethyladamantane-1,3-dicarboxylic acid and 3,3′-dihydroxybenzidine have unusual properties[109]:



The prepolymer obtained in the first stage with η_{ln} = 1.13 gives rise to a colourless film soluble in water on pressing at specified temperatures. Thermal cyclisation of the film with a stepwise increase of temperature from 150° to 350 °C yielded a colourless polybenzoxazole soluble in water. The film has σ_t = 1.2 MPa and E_e = 210 MPa, losing ~ 10% of its weight on heating to 500 °C.

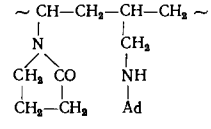
The synthesis of a polybenzimidazole from the diphenyl ester of adamantanedicarboxylic acid and 3,3′-diaminobenzidine has been described[110]:



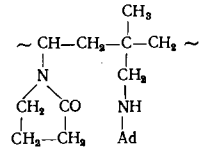
The polymer has a low molecular weight (η_{ln} = 0.19) and is soluble in DMF and dimethyl sulphoxide (DMSO), but its thermal stability is lower than that of aromatic polybenzimidazoles: it begins to decompose in nitrogen at 540 °C.

VIII. BIOLOGICALLY ACTIVE ADAMANTANE-CONTAINING POLYMERS

Progress in the chemistry of adamantane is to a large extent associated with the biological activity of some of its functional derivatives[6,21]. However, only a few studies have been made on the polymeric adamantane derivatives used in medicine. The copolymers of *N*-vinylpyrrolidinone and *N*-allylaminoadamantane[111]

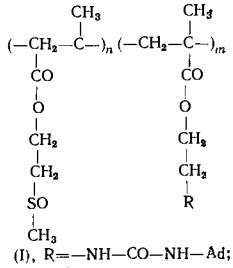


as well as the reduced products of the interaction of 1-aminoadamantane and the copolymer of *N*-vinylpyrrolidinone and crotonaldehyde[111], i.e.



have been proposed as potential antiviral agents. Water-soluble 2-(methylsulphinyl)ethyl methacrylate–2-*N*-(1′-adamantyl)ureidoethyl methacrylate (I) and the quarternary

ammonium salts of *N*-(1-adamantyl)chloroacetamide–2-dimethylaminoethyl methacrylate (II) copolymers have been described in another study[112]:

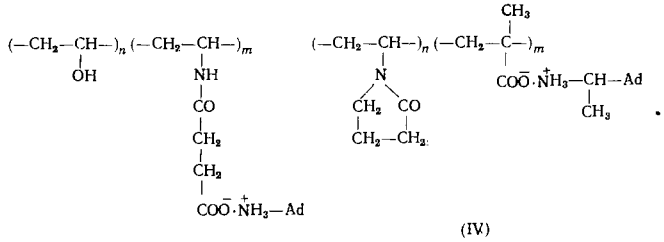


(I), R=—NH—CO—NH—Ad;

(II), R=—$\overset{+}{N}(CH_3)_2$—CH_2CONH—Ad .

It was found that only copolymer (II), containing ammonium groups, exhibits an antiviral activity.

Polymeric complexes of the salt type, obtained by treating with 1-aminoadamantane (III) and 1-(2′-aminoethyl)adamantane (IV) the copolymers of poly(vinyl alcohol) and *N*-vinylpyrrolidinone with *N*-vinylamidosuccinic and crotonic acids, have been studied in greater detail[113,114]:



(IV)

The study of the polymeric products showed that they are less toxic than the hydrochlorides of amino-derivatives of adamantane and that their prophylactic effect lasts five times longer. Two medicinal preparations with prolonged antiviral activity have been developed on their basis.

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Analysis of published data permits the definite conclusion that the introduction of the polyhedral adamantane molecule into polymers significantly improves some of their properties. The vast majority of adamantane-containing polymers are heat-resistant and soften at high temperatures. An important feature of these polymers is their high resistance to oxidation and hydrolysis and to the action of light and solvents. The properties of adamantane-containing polymers are superior to those of familiar industrial polymers and can find applications in various branches of technology.

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Monometal Hydrido-complexes of Transition Metals

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Published information on the chemistry of these complexes stabilised by cyclopentadienyl and other ligands is systematised, and modes of formation of a metal-hydrogen bond in their synthesis are discussed. Consideration is given to the influence on this bond of the structure of various types of transition-metal hydrides containing one, two, or three cyclopentadienyl groups in the coordination sphere. The possibility of stabilising the bond with σ-donor ligands is discussed. The chemical properties of these compounds and the possibility of their use as catalysts are examined. A list of 160 references is included.

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I. INTRODUCTION

Intensive research has been undertaken during recent years on the preparation and properties of molecular hydrides of transition metals. The unfailing interest taken in them is associated with the development of modern views on the nature of the chemical bond and the stereochemistry of complexes containing a hydrido-ligand, as well as the theory and practice of homogeneous and heterogeneous catalysis of the reactions of unsaturated compounds. One of the most interesting and least studied aspects is catalysis on systems of the Ziegler–Natta type. Hydrido-complexes containing a transition metal together with a non-transition metal can be taken as models of the active centres in these systems. In most cases such complexes can be regarded as derivatives of individual transition-metal hydrides.

The most effective electron-donor ligands stabilising a metal–hydrogen bond are π-accepting (carbonyl, nitrosyl, phosphines, phosphites, arsines, etc.) and π-donor groups (η-cyclopentadienyl, related groups, and to a less extent arsines). π-Accepting ligands form coordinatively saturated mononuclear compounds (phosphorus- or arsenic-containing hydrides) or cluster compounds (carbonyl hydrides), which with rare exceptions do not yield complexes with compounds of non-transition metals, Lewis acids. These hydrides have been studied in some detail, and surveyed in reviews[1–5].

Most of the dimetal hydrido-complexes reported contain cyclopentadienyl ligands. Dicyclopentadienyl hydrides of transition metals have been covered in previous reviews[1,6,7]. During the past five to six years, however, results of fundamental importance have been obtained on the structure of known compounds of this type and on the synthesis of new ones, especially dinuclear complexes containing ($\eta:\sigma=C_5H_4$) groups or a fulvalene ligand (η-C_5H_4–η-C_5H_4). In this connection definite interest attaches also to the less stable monocyclopentadienyl hydrides of type $C_5H_5ML_3H_n$ and $C_5H_5ML_2H_n$, which are isoelectronic with the dicyclopentadienyl hydrides $(C_5H_5)_2M'H_n$, as well as the recently prepared transition-metal hydrides stabilised with σ-donor ligands (groups containing nitrogen or oxygen).

Hydrides have been described containing one, two, or three cyclopentadienyl groups attached to a transition-metal atom. The most stable and most thoroughly studied are dicyclopentadienyl hydrides, which can be subdivided into two main groups—the true dicyclopentadienyl hydrides of general formula $(\eta\text{-}C_5H_5)_2MH_n$ ($n = 1–3$) and the so called bismetallocene hydrides—in the latter of which the metal–hydrogen bond is formed by rearrangement, accompanied by dimerisation, in an unstable metallocene $(C_5H_5)_2M$ with migration of hydrogen from a cyclopentadienyl group to the metal atom. Dimerisation is effected either through a bridging fulvalene ligand η-C_5H_4–η-C_5H_4 (structures of the "stable titanocene" type[8]) or by two $\eta:\sigma=C_5H_4$ groups (structures of niobocene type[9]).

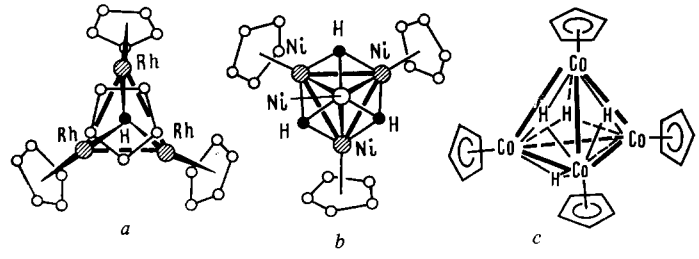


Figure 1. Structure of monocyclopentadienyl hydrides: *a*) $(C_5H_5)_4Rh_3H$;[10] *b*) $(C_5H_5)_4Co_4H_4$;[11] *c*) $(C_5H_5)_4Ni_4H_3$.[12]

The unstable monocyclopentadienyl hydrides of transition metals are stabilised either by the addition of two-electron and in some cases one-electron ligands or by the formation of clusters, among which $(C_5H_5)_4Rh_3H$,[10] $(C_5H_5)_4Co_4H_4$,[11] and $(C_5H_5)_4Ni_4H_3$[12] are known. In all these compounds the hydrogen atoms are attached to three transition-metal atoms, and are located above the plane of the triangle formed by the latter (Fig.1). Stabilisation by means of electron-donor ligands results in the formation of complexes of type $C_5H_5M(ArH)H_n$, $C_5H_5ML_3H_n$, $C_5H_5ML_2H_n$, and $C_5H_5MLXH_n$, where $n = 1–3$, L is a two-electron ligand, and X a one-electron ligand. These compounds are isoelectronic with dicyclopentadienyl hydrides $(C_5H_5)_2MH_n$ of the metals on the right or on the left in the Periodic Table.

Descriptions have appeared not only of neutral cyclopentadienyl hydrides but also of anionic (of metals in Groups IV and V) and cationic (in Groups VI–VIII) complexes.

II. METHODS OF PREPARATION OF CYCLOPENTADIENYL HYDRIDES OF TRANSITION METALS

Methods of obtaining cyclopentadienyl hydrides are in general the same as those for other transition-metal hydrides stabilised with π-accepting ligands. Possible sources of hydrido-hydrogen are molecular hydrogen, cyclopentadienyl groups, hydrides and alkyl compounds of non-transition metals and boron, compounds containing mobile hydrogen atoms, in particular Brønsted acids, and also apparently solvent molecules in certain cases. Our survey of general methods for synthesising cyclopentadienyl hydrides of transition metals will be based on the classification suggested in Ref.7†.

1. Reactions with Molecular Hydrogen

(1a) Oxidative addition

Hydrogen adds reversibly to permethyltitanocene to give the corresponding titanium(IV) dihydride[13]:

$$(C_5Me_5)_2Ti + H_2 \rightleftarrows (C_5Me_5)_2TiH_2 . \qquad (1)$$

Chromocene reacts with carbon monoxide and hydrogen under high pressures to yield[14] $C_5H_5CrH(CO)_3$. Formation of an anionic complex $Na^+(C_5H_5)_2TiH_2^-$ in the system comprising dicyclopentadienyltitanium dichloride with sodium naphthalide in an atmosphere of hydrogen also probably involves oxidative addition of hydrogen to unstable dicyclopentadienyltitanium followed by reduction[15].

We may note also the displacement of π-bonded ligands by hydrogen, reported for dinitrogen complexes of zirconium (II)[16] and molybdenum(0)[17]:

$$[(C_5Me_5)_2Zr(N_2)]_2N_2 + H_2 \xrightarrow[25°C]{\text{toluene}} (C_5Me_5)_2ZrH_2 + N_2 .$$

(1b) Hydrogenolysis of Metal–Carbon σ-bond

In some cases a metal–alkyl bond is very readily split by hydrogen with formation of metal–hydrogen bond. Thus dicyclopentadienyldimethyltitanium reacts with hydrogen even under low pressures, but the reaction becomes explosive when the pressure is raised above 250 mmHg[18] [Cp = C_5H_5]:

$$2Cp_2TiMe_2 + 3H_2 \xrightarrow[pH_2 \leqslant 250\ mmHg]{\text{solid phase}} (Cp_2TiH)_2 + 4CH_4 .$$

A similar reaction has been reported for bispentamethylcyclopentadienyldimethyl compounds of uranium and thorium[19]:

$$2(C_5Me_5)_2MMe_2 + 4H_2 \xrightarrow[25°C]{\text{toluene}} [(C_5Me_5)_2MH_2]_2 + 4CH_4 .$$

(1c) Hydrogenolysis of Metal–Metal Bond

Fission of a metal–metal bond by hydrogen has been reported only for cyclopentadienyl carbonyls of Group VI metals. Tricarbonylcyclopentadienylchromium hydride is formed[20] by the action of hydrogen on bis(tricarbonylcyclopentadienylchromium) at 150 atm and 70 °C. The corresponding reaction with the molybdenum compound takes place under still more severe conditions[14].

2. Oxidative Addition of H–Z Compounds

Compounds containing a sufficiently mobile hydrogen atom can add to low-valency transition-metal complexes to form M–H and M–Z bonds. The H–Z compounds may be hydrocarbons or hydrides of elements of the germanium subgroup.

(2a) Oxidative Addition of Hydrocarbons

Reduction of dicyclopentadienylzirconium dichloride with metallic sodium in the presence of naphthalene in oxolan forms a naphthyl hydrido-complex

$$(C_5H_5)_2Zr\mu(H)\mu(2\eta^1 : 2\eta^2\text{-}C_{10}H_7)Zr(C_5H_5)_2$$

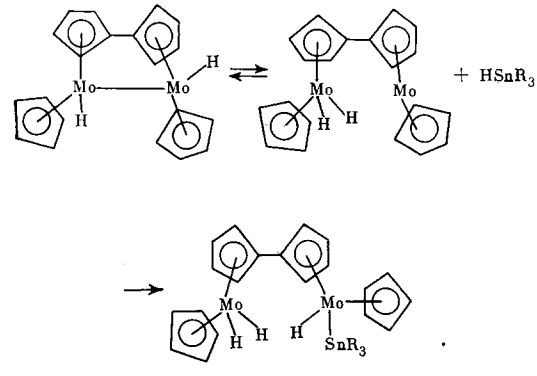
apparently by addition of naphthalene to the metastable dicyclopentadienylzirconium[21].

Cyclopentadienyl hydrides of transition metals have been obtained also by the oxidative addition of cyclopentadiene. Thus photoreaction of the latter with $C_5H_5Nb(P(C_6H_5)_3)_2(CO)_2$ gives the dihydride $C_5H_5Nb(P(C_6H_5)_3)_2(CO)H_2$, which is isoelectronic with $(C_5H_5)_2MoH_2$.[22] An analogous reaction has been reported for $Ni(P(C_6H_{11})_3)_2$[23] and $M(CO)_3(NCCH_3)_3$, where M = Cr, Mo, W.[24–26] The respective reaction products are $C_5H_5NiP(C_6H_{11})_3H$ and $C_5R_5M(CO)_3H$ (R = H, CH_3).

The action of atomic molybdenum and tungsten on excess of cyclopentadiene forms the dicyclopentadienyl dihydrides, with yields of 40–50% from the latter metal. Subliming the products of the reaction of atomic tungsten with a mixture of cyclopentadiene and an arene gives the complexes $C_5H_5W(ArH)H$.[27]

(2b) Oxidative Addition of Hydrides of the Germanium Subgroup

The photochemical action of trichlorosilane on cyclopentadienyl carbonyls of manganese, iron, and cobalt and also on arene carbonyls of chromium is accompanied by the evolution of carbon monoxide and the formation of cyclopentadienyl hydrides containing a metal–silicon bond[28]. The action of trialkylstannanes on $(C_5H_5MoH)_2(C_5H_4\text{–}C_5H_4)$ yields $C_5H_5MoH_2\text{-}\mu\text{-}(C_5H_4)C_5H_5Mo(H)SnR_3$, probably by oxidative addition to molybdenum(II)[29]:



† The numbering in the columns denoting "preparation" in Tables 1, 5, and 7 corresponds to the subheadings in this Section.

3. Protonation of Cyclopentadienyl Compounds of Transition Metals

Cyclopentadienyl hydrides of Groups VI–VIII transition metals possess lone pairs of electrons, and react with Brønsted acids to form metal–hydrogen bonds (oxidative addition of protons). The acids usually employed are tetrafluoroboric, hexafluorophosphoric, concentrated sulphuric, and anhydrous hydrohalic. Protonation of neutral complexes yields cationic hydrides. Dicyclopentadienyl hydrides $(C_5H_5)_2MH_n$ (M = Mo, W, Re, Tc) and also ferrocene give stable ionic complexes $(C_5H_5)_2MH_{n+1}^+X^-$. The carbonyl complexes $C_5H_5W(CO)_2H$[30] and $C_5H_5Ir(CO)_2P(C_6H_5)_3$[31] undergo analogous reactions, forming unstable hydrido-cations. Protonation accompanied by ligand substitution has been reported[32]:

$$CpRh(C_2H_4)_2 + BF_3\cdot H_2O + PPh_3 \xrightarrow{CH_3OH} [CpRh(PPh_3)_2H]^+[BF_4]^- .$$

Protonation of dinuclear cyclopentadienyl carbonyls of transition metals yields dinuclear hydrido-complexes $[C_5H_5M(CO)_3]_2H^+X^-$ (M = Mo, W) and $[C_5H_5M(CO)_2]_2H^+X^-$ (M = Fe, Ru).[30] A complex $[(C_5H_5)_2WH]_2H^+ClO_4^-$ has been obtained by the cathodic reduction of dicyclopentadienyltungsten dihydride in acetonitrile[33]. All these complexes apparently[33] contain a linear M–H–M bridge.

Anionic cyclopentadienyl carbonyls of molybdenum and tungsten also undergo protonation, forming neutral hydrides. Deuteroacetic acid yields the corresponding deuterides[14–34]:

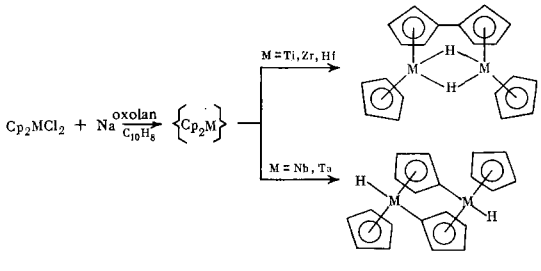
$$CpM(CO)_3^-Na^+ + CH_3COOD \rightarrow CpM(CO)_3D + CH_3COONa$$
$$M=Mo, W .$$

4. Reduction of Cyclopentadienyl Compounds of Transition Metals

Mild reduction of dicyclopentadienyl hydrides $(C_5H_5)_2MH_n$ (n = 2,3) in some cases yields the compounds $(C_5H_5)_2MH_{n-1}$. Further reduction results in unstable metallocenes $(C_5H_5)_2M$, which undergo rapid rearrangement with incorporation of metal at a carbon–hydrogen bond of a cyclopentadienyl group to give dimeric bismetallocene hydrides.

(4a) Reduction by Alkali Metals

Reduction of dicyclopentadienyl dichlorides $(C_5H_5)_2MCl_2$ by alkali metals (sodium and to a less extent potassium) in the form of amalgams or naphthalene complexes is the principal method of preparation of bismetallocene hydrides of titanium[35–37], zirconium and hafnium[38,39], and niobium and tantalum[9,40]:



This reaction can be accomplished with catalytic quantities of naphthalene[39]. At −80 °C it leads to formation of the complex $C_5H_5Ti\mu$-(σ : η-C_5H_4)$Ti(C_5H_5)_2.C_4H_8O$,[41] treatment of which with toluene gives the non-solvated complex. A titanium–hydrogen bond may[41] be present. Intermediate formation of monomeric $(C_5H_5)_2M$ has been demonstrated by electron spin resonance in the case of niobocene[40]. Treatment of niobocene $C_5H_5Nb(H)(\mu = C_5H_4)_2Nb(H)(C_5H_5)_2$ with sodium naphthalide gives the anionic complex $Na_2[C_5H_5Nb(H)\mu$-$C_5H_4]_2$.[42] An analogous reaction has been reported for the titanium compounds $(C_5H_5)_2TiR_2$.[43]

(4b) Photochemical and Thermal Decomposition of Dicyclopentadienyl Hydrides and Alkyls of Transition Metals

Photolysis and thermal decomposition of $(C_5H_5)_2MR_2$ (M = Ti, Zr) and $(C_5H_5)_2MH_2$ (M = Mo, W) lead to the formation of bismetallocene hydrides. The course of the reaction and the composition of the final products are significantly influenced by the nature of the solvent.

Thermolysis of $(C_5H_5)_2MR_2$ (M = Ti, Zr, V) is usually accompanied by migration of hydrogen atoms of the cyclopentadiene ring to transition-metal atoms and elimination of an RH group[44–47]. A mixture of products is formed, containing π,σ-bound C_5H_4 groups and perhaps metal–hydrogen bonds[45]. Partial retention of the dicyclopentadienyl structure has been noted only with vanadium[47]. In contrast to thermolysis, the photolysis of $(C_5H_5)_2Ti(C_6H_5)_2$ has a radical mechanism[48]. In solvating solvents dicyclopentadienyltitanium hydride is formed, but in inert solvents the metastable dicyclopentadienyltitanium, which in an atmosphere of carbon monoxide is converted into the carbonyl $(C_5H_5)_2Ti(CO)_2$.[48]

Exposure (λ = 366 nm) of an iso-octane solution of $(C_5H_5)_2MoH_2$ gives a polymeric product $[(C_5H_5)_2Mo]_x$ of undetermined structure[49]. Replacement of iso-octane by ethanol[50] or toluene[51] as solvent yields a dinuclear compound

$$C_5H_5Mo\mu\text{-}[\sigma : \eta\text{-}C_5H_4)_2MoC_5H_5$$

perhaps by stabilisation of the intermediate monomeric compound $(C_5H_5)_2Mo$ by the solvent. Photolysis of $(C_5H_5)_2WH_2$ in diethyl ether gives $(C_5H_5WH)_2\mu = (\sigma : \eta = C_5H_4)_2$, but in tetramethylsilane *cis*- and *trans*-$(C_5H_5WH)\mu$-(σ : η-$C_5H_4)_2$. .$(C_5H_5WCH_2Si(CH_3)_3)$ are formed[50,51]. Furthermore, the thermal decomposition of $(C_5H_5)_2W(CH_3)H$ in cyclohexane yields the isomers $(C_5H_5WH)\mu$-(σ : η-$C_5H_4)_2(C_5H_5WCH_3)$.[51]

(4c) Cathodic and Other Reductions

Tervalent tungsten hydride $(C_5H_5)_2WH$ has been obtained as a complex with phenanthraquinone by electrolysis of $(C_5H_5)_2WH_2$ at a controlled potential. The cations $[(C_5H_5)_2W(R)H]^+$ and $[((C_5H_5)_2WH)_2H]^+$ have been obtained similarly[33].

Niobium(IV) and tantalum(IV) hydrides identified by electron spin resonance, have been obtained[52] by treating the $(C_5H_5)_2MH_3$ with di-t-butyl peroxide:

$$Cp_2NbH_3 + BuO^\cdot \xrightarrow[-80^\circ C]{h\nu} Cp_2NbH_2 + BuOH .$$

(4d) Reactions of Compounds of Transition Metals in Lower States of Oxidation

Double decomposition between cyclopentadienylsodium and low-valency transition-metal compounds can be used to obtain bismetallocene hydrides with intermediate formation of the dicyclopentadienyl compounds. Thus reactions involving titanium(II) chloride and dimeric molybdenum(II) acetate

yield fulvalene complexes containing methyl–hydrogen bridges (in the case of titanium)[53] and terminal bonds (molybdenum)[54].

5. Use of Alkyl and Hydride Compounds of Non-transition Metals and of Boron

Alkyl and hydride derivatives of Groups I–III metals (usually lithium, magnesium, or aluminium) and also hydroborates are the most frequent reactants for obtaining cyclopentadienyl hydrides of transition metals. The most convenient are hydro-aluminates and -borates, mostly solutions of lithium tetrahydroaluminate in ether or oxolan or of sodium tetrahydroborate in alcohol. The recent availability of new reagents such as $NaBH(C_2H_5)_3$, $LiAlH(OC_4H_9\text{-}t)_3$, and $NaAlH_2(OCH_2CH_2OCH_3)_2$ has extended significantly the range of solvents employed (in particular to aromatic hydrocarbons) and the overall possibilities of the method. The starting materials usually employed are transition-metal complexes containing bonds between metal and halogen or pseudohalogen, which is exchanged for an ElH_4^- group or a hydride anion. In all cases the reaction involves intermediate formation of more or less stable dimetal complexes containing M–C–El or M–H–El bridges. A metal–hydrogen bond is formed by three principal mechanisms—elimination of an alkene from a metal–carbon σ-bond, homolytic elimination of a hydro-borate or -aluminate group ElH_4^-, and hydrolysis of M–H–El bridges or direct M–El bonds.

(5a) Elimination of Alkene from Alkyl–Metal Complexes

In the reaction between dicyclopentadienyltitanium di- or mono-chloride and organo-lithium or -magnesium compounds electron spin resonance has revealed the presence in solution of anionic complexes $(C_5H_5)_2TiH_2^-M^+$ (M = Li, Na, MgX)[55–57]. The hydrogen originates in alkyl groups[57].

Successive treatment of $C_5H_5Co(P(CH_3)_2C_6H_5)I_2$ with isopropylmagnesium bromide and hexafluorophosphoric acid in oxolan gives the cationic complex $[C_5H_5Co(P(CH_3)_2C_6H_5)H]^+.[PF_6]^-$.[58] The tetraphenylcyclobutadiene complex $C_5H_5Mo(CO)(C_4(C_6H_5)_4)H$ is obtained similarly[59]. An unusual photochemical reaction of tungsten hexachloride with cyclohexa-1,3-diene, cyclopentadienylmagnesium bromide, and isopropylmagnesium bromide in ether yields the complex $C_5H_5W(\eta\text{-}C_6H_6)H$.[60]

(5b) Splitting of Tetrahydro-borate and -aluminate Groups

The action of hydroborates and especially of alkali-metal hydroaluminates on complexes of transition metals in higher states of oxidation usually involves reduction of the transition metal (except zirconium). Thus the reaction of triscyclopentadienyluranium monochloride with lithium triethylhydro-borate or tetrahydroaluminate yields solvated triscyclopentadienyluranium, presumably via an unstable intermediate $(C_5H_5)_3UH.L$.[61]

The complicated reaction of higher chlorides of niobium, tantalum, molybdenum, tungsten, rhenium, and technetium with the tetrahydroborate and the cyclopentadienyl of sodium in oxolan provides a general method for obtaining dicyclopentadienyl hydrides of those metals[62–65]. Although it requires precise observance of the procedure, it does not always give high yields. Application to the preparation of dicyclopentadienylniobium trihydride requires a high pressure of hydrogen (800 atm) over the reaction mixture[63], but that of dicyclopentadienyl-molybdenum or -tungsten dihydride needs low temperatures of −(100–120) °C. Sodium tetrahydroborate has been used to obtain dicarbonylcyclopentadienyl-iron and -ruthenium monohydrides[66,34] from corresponding halides.

In some cases the transition-metal cyclopentadienyl tetrahydroborates formed undergo homolytic fission only under the influence of stronger Lewis bases:

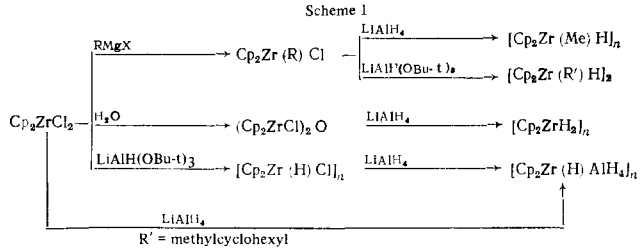
$$Cp_2M\left(\begin{smallmatrix} H & & H \\ & B & \\ H & & H \end{smallmatrix}\right)_n + n\,L \rightarrow Cp_2MH_n + n\,BH_3\cdot L\ .$$

Thus dicyclopentadienylzirconium bistetrahydroborate forms the corresponding hydrido-monotetrahydroborate in the presence of an equimolecular quantity of trimethylamine, and the dihydride $[(C_5H_5)_2ZrH_2]_x$ with double that quantity[67]. Dicyclopentadienyltitanium tetrahydroborate does not undergo this reaction[67], although the tetrahydroborate group is decomposed by triethylamine in the presence of carbon monoxide, when dicarbonyldicyclopentadienyltitanium is obtained[68]. Use of excess of phosphine (phosphite) for this purpose yields phosphorus-containing hydrides: thus for the monocyclopentadienylchromium complex[69]

$$CpCrCl_2\cdot C_4H_8O \xrightarrow[\text{oxolan}]{NaBH_4} CpCr(BH_4)_2 \xrightarrow{P(OMe)_3} CpCr[P(OMe)_3]_3H\ .$$

Several dicyclopentadienyl hydrides of zirconium(IV) have been obtained by the action of lithium tetrahydroaluminate or tri-t-butoxyhydroaluminate on chlorine-containing complexes[70,71] (Scheme 1).

Scheme 1



The complexes $C_5H_5M(NO_2)H$ (M = Mo, W) have been obtained by treating the corresponding chlorides with sodium bismethoxyethoxydihydroaluminate in toluene[72]. An analogous method has been used to prepare $C_5H_5Mo(C_6H_6)H$[73] and $C_5H_5Mo(diphos)H_3$.[74] In several cases the resulting transition-metal (titanium, niobium, etc.) hydroaluminates are not decomposed by the solvent with formation of a metal–hydrogen bond and a solvated aluminium hydride: thus the TiH_2Al link is not broken even by triethylamine[75]. Conducting the reaction between dicyclopentadienyltitanium dichloride and lithium tetrahydroaluminate in non-solvating solvents (alkenes) gives fulvalene hydrides $(\eta\text{-}C_5H_4\text{–}\eta\text{-}C_5H_4)(C_5H_5Ti.(X)(Y)TiC_5H_5)$, where X, Y = H, Cl.[76]

A heterogeneous exchange reaction with sodium hydride has also been described. Thus triscyclopentadienyl- and also bisindenyl-cerium(IV) hydrides have been obtained from the chlorides heated in oxolan at 100 °C for 5–6 h.[77]

(5c) Hydrolysis of Compounds Containing Metal–Hydrogen–Element and Metal–Element Bonds

Reaction between $(C_5H_5)_2NbCl_2$ and $NaAlH_2X_2$ (X = H, C_2H_5, $CH_3OCH_2CH_2O$) gives an equimolecular mixture of $(C_5H_5)_2NbH_3$ and $(C_5H_5)_2NbH_2AlX_2$.[78] When X = H, only $(C_5H_5)_2NbH_2AlH_2$ is formed in the course of time, but conducting the reaction in the presence of carbon monoxide, a

trialkylphosphine, or ethylene gives the $(C_5H_5)_2Nb(H)L$ in at most 50% yield (trialkylphosphines do not react with $(C_5H_5)_2NbH_2AlH_2$). This reaction is assumed to involve disproportionation of the niobium(IV) dihydride[78]:

$$Cp_2NbCl_2 + NaAlH_4X_2 \xrightarrow[-NaCl,\ -AlHX_2]{\text{oxolan}} Cp_2NbH_2 \begin{cases} \longrightarrow Cp_2NbH_3 \\ \longrightarrow Cp_2NbH \xrightarrow{AlHX_2} Cp_2NbH_2AlX_2 \end{cases}$$

Hydrolysis of the reaction mixture and also of the individual $(C_5H_5)_2NbH_2AlH_2$ gives high yields of $(C_5H_5)_2NbH_3$. Hydrolysis takes place unsymmetrically: reaction with deuterium oxide yields $(C_5H_5)_2NbH_2D$ isomers and deuteroxy-groups attached to the aluminium atom[78].

Mild hydrolysis of the complex $[C_5H_5Ti\mu\text{-}(H)\mu\text{-}(H_2Al.(C_2H_5)_2)TiC_5H_5](C_{10}H_8)$ gives a 70% yield of stable titanocene[79]. The cation $(C_{10}H_8)(C_5H_5Mo(H)(OH)MoC_5H_5)^+$ has been obtained by treating "bismetallocene hydrides" of molybdenum with aqueous hexafluorophosphoric acid[51,80]. Transition-metal cyclopentadienyl hydrides are formed not only by hydrolytic fission of bridging hydrogen bonds but also by the fission of bonds between the transition metal and a non-transition metal, when hydroxo-groups combine with the more electropositive atom. Thus hydrolysis of the molybdenum complexes $[(C_5H_5)_2Mo(H)Li]_4$ $(C_5H_5)_2Mo(H)MgBr.2C_4H_8O$, and others containing molybdenum–magnesium and molybdenum–aluminium bonds gives high yields of $(C_5H_5)_2MoH_2$.[81–83] A similar reaction has been reported for $(C_5H_5)_2Ta(H)_2Li$.[84]

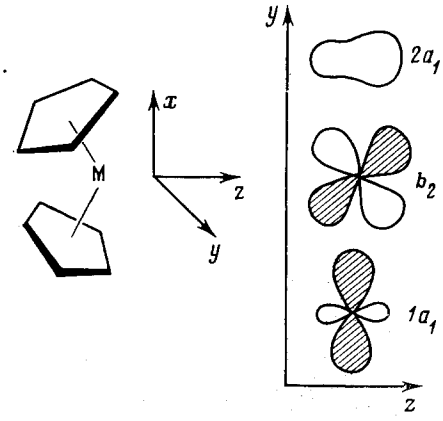


Figure 2. Schematic representation of valency orbitals of the metal atom in the $(C_5H_5)_2M$ group.[88]

Table 1. Physicochemical properties of dicyclopentadienyl hydrides of transition metals.

Compound	Prep.	M.p., °C (decomp., °C)	Solvent	ν(M–H) (ν(M–D)), cm^{-1}	τ_{M-H}, ppm A	τ_{M-H}, ppm B	Ref.
$(Cp_2TiH)_2$	1b	(>70)	Et_2O, oxolan(—70°)	1450(1260, 1050)	—	—	[18]
$(Cp_2TiH)_x$	1b	(>60)	*	1140(800—850)	—	—	[18, 89]
$(Cp_2TiN)_2H_3$	2		PhMe	1585**	—	—	[90]
$(Cp_2ZrH_2)_x$	1b	(120)	*	1520, 1300 (1100, 960)	—	—	[67, 91]
$[Cp_2Zr(R)H]_2$***	5b	—	C_6H_6, Et_2O	1500, 1313	12.35	—	[71]
$Cp_2Zr(H)BH_4$	5b	—	C_6H_6	1945	5.47	—	[67]
$[Cp_2Zr(H)AlH_4]_x$	5b	(>60)	*	—	—	—	[70]
$Cp_2Zr(H)(C_{10}H_7)ZrCp_2$	2a	—	oxolan	—	19.3	—	[21]
Cp_2NbH_3	5b, 5c	(>80)	C_6H_6	1710	12.73	13.72	[63]
Cp_2TaH_3	5b, 5c	(>80)	C_6H_6	1735	11.63	13.02	[84, 92]
Cp_2MoH_2	5b	183—185	C_6H_6, oxolan	1853	—	18.17	[62, 93, 94]
Cp_2WH_2	5b	163—165	C_6H_6, oxolan	1912	—	22.28	[62, 93, 94]
$Cp_2W(H)GePh_3$	5b	235	—	—	21.50	—	[95]
$Cp_2W(H)SnPh_3$	5b	209	—	—	22.24	—	[95]
$Cp_2W(H)PbPh_3$	5b	(198)	—	—	22.78	—	[95]
$Cp_2WH_3{}^+Cl^-$	3	—	—	1943	16.08	16.44	[34]
$[(Cp_2W)_2H_3]^+ClO_4^-$	4c	—	—	2030	26.2	—	[33]
Cp_2TcH	5b	130—155	oxolan C_6H_6, hexane	1923	17.8	—	[65]
$[Cp_2TcH_2]^+PF_6^-$	3	—	—	1984	—	19.7	[65]
Cp_2ReH	5b	161—162	oxolan C_6H_6	2032, 2000	23.0	—	[65, 93]
$[Cp_2ReH_2]^+PF_6^-$	3	—	—	2058	24.6	—	[65]
$[Cp_2ReH]^+AlCl_4^-$	3	(125)	—	—	—	—	[96]
$(C_5Me_5)_2TiH_2$	1a	(>25)	C_6H_6, heptane	1560	—	—	[13]
$(C_5Me_5)_2ZrH_2$	1a	—	C_6H_6, heptane	1555(1100)	—	—	[16]
$[(C_5Me_5)_2UH_2]_2$	1b	(>20)	PhMe	1215, 1114(873, 802)	—	—	[19]
$[(C_5Me_5)_2ThH_2]_2$	1b	—	PhMe	1406, 1361(1020, 979)	—	—9.25	[19]

* Almost insoluble in organic solvents.
** Probably ν(M–H–N) absorption band.
*** R = methylcyclohexyl.

III. TRANSITION-METAL HYDRIDES STABILISED WITH CYCLOPENTADIENYL σ-DONOR AND LIGANDS

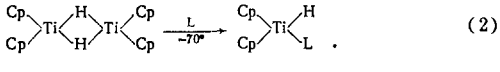
1. Dicyclopentadienyl Hydrides of Transition Metals

Quantum-chemical calculations indicate that the metal atom associated with the inclined rings in $(C_5H_5)_2ML_n$ molecules ($n = 1-3$)[85-88] has three hybrid orbitals, used in forming bonds with ligands and lying in the plane of symmetry yz. According to modern views[87,88] these orbitals have the form depicted in Fig.2. The highest is the $2a_1$ orbital. In the case of a single σ-bonding ligand such as hydrido, with orbitals $1a_1$ (and b_2) filled with electrons, a symmetrical structure is observed with the ligand located on the z axis. In the case of unfilled orbitals overlapping with lower orbitals is energetically more favourable, and the ligand is located between y and z axes[88]. When two ligands are present, the $2a_1$ and b_2 orbitals give two equivalent molecular orbitals, which is closely similar to Alkock's model[86]. With $n = 3$ the ligands form an AB_2 system, which is consistent with the earlier model of Ballhausen and Dahl[85]. Most of the compounds studied conform to the eighteen-electron rule[88].

The complexes $(C_5H_5)_2MH_n$ ($n = 1-3$) are typical covalent compounds. Their physicochemical properties are listed in Table 1.

Group IV

Dicyclopentadienyltitanium(III) hydride exists in two modifications: the grey–green form is polymeric[89], and the violet form apparently dimeric[18]. Association of the electron-deficient $(C_5H_5)_2TiH$ molecules is facilitated by energetic factors[88], and is apparently effected by hydrogen bridges. Absorption bands due to terminal titanium–hydrogen bonds are absent from the infrared spectra, but bands at 1450 and 1140 cm^{-1} are assigned to unsymmetrical stretching vibrations of Ti–H–Ti bridges in dimer and polymer respectively[18]. The action of electron donors (oxolan, triphenylphosphine) stronger than hydride hydrogen results in homolytic fission of hydrogen bridges and formation of unstable monomeric hydrides $(C_5H_5)_2Ti(H)L$:[18]



(2)

The presence of a vacant orbital is the obvious reason why dicyclopentadienylzirconium(IV) hydride $(C_5H_5)_2ZrH_2$ and the related compounds $(C_5H_5)_2Zr(H)X$ (X = Cl, CH_3, AlH_4) are formed as polymers. They are almost non-volatile and insoluble in organic solvents[67,70], except in the cases of the sterically hindered $(C_5H_5)_2Zr(H)R$ (R = methylcyclohexyl)[71] and $(C_5H_4C(CH_3)_3)_2ZrH_2$ (dimer in benzene).[91] The vibrational bands due to the metal–hydrogen bond in the compounds correspond to bridging hydrogen atoms (Table 1): they are located at 1390 cm^{-1} for X = Cl, and at 1500 and 1310 cm^{-1} for X = CH_3.[70] The compound $(C_5H_5)_2Zr(H)BH_4$ is a monomer containing terminal zirconium–hydrogen bonds[67].

Absorption bands ν(Zi–H) are absent[21] from the infrared spectrum of the dinuclear naphthyl hydrido-complex

$$(C_5H_5)_2\overline{Zr\mu\text{-}(H)\mu\text{-}(2\text{-}\eta^1:1\text{-}2\eta^2\text{-}C_{10}H_7)Zr}(C_5H_5)_2 .$$

X-Ray determination of the structure (Fig.3*a*) could not locate the hydrogen atom[21], but its presence follows from stereochemical considerations, nuclear magnetic resonance data (Table 1), and chemical properties (reactions with iodomethane and hydrogen chloride)[21,97].

The unusual complex $((C_5H_5)_2TiN)_2H_3$ is obtained by treating $(C_5H_5)_2Ti\mu(\sigma:\eta\text{-}C_5H_4)TiC_5H_5$ with ammonia, when one mole of hydrogen is evolved, or with a primary or secondary amine[90,98]. X-Ray structural analysis indicates[90] that a molecule of the complex contains the usual wedge-shaped $(C_5H_5)_2Ti$ sandwiches and a planar metal ring TiN_2Ti (the hydrogen atoms could not be located). A band at 1585 cm^{-1}, which is displaced when nitrogen-14 is replaced by nitrogen-15 and hydrogen by deuterium in the original ammonia, is apparently due to vibration of a Ti–H–N bond. The chemical properties of the complex undoubtedly indicate the hydride character of all the hydrogen atoms not present in cyclopentadienyl groups[99]. This, together with the presence of only one unpaired electron per molecule, suggested[90] that the hydrido-atoms were present at the positions indicated in Fig.3*b*.

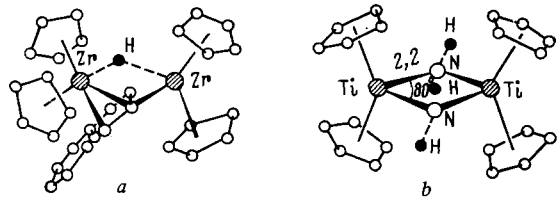


Figure 3. Molecular structure of: *a*) $(C_5H_5)_2\overline{Zr(H)(C_{10}H_7)Zr}.(C_5H_5)_2$;[21] *b*) $((C_5H_5)_2TiN)_2H_3$.[90]

Besides neutral dicyclopentadienyltitanium(III) hydrides electron spin resonance has detected the formation of anionic complexes $(C_5H_5)_2TiH_2^-M^+$ (M = Li, Na)[55-57,100] and $(C_5H_5)_2.TiHCl^-M^+$.[15] The Ti–H–M bond in them is largely covalent in character, the degree of covalency increasing in the sequence Na < Li < MgX < $AlCl_2$ < AlH_2.[100]

The parameters of the e.s.r. spectra of dicyclopentadienyltitanium(III) hydrides are listed in Table 2. The e.s.r. method is extremely useful also for investigating paramagnetic dicyclopentadienyl hydrides of other transition metals, in particular of niobium(IV) and tungsten(III) (below), which exist only in solution.

The dicyclopentadienyl trihydrides of niobium and tantalum are quite similar in properties, differing only in reactivity: the former is far more active than the latter, which is consistent with the fairly severe conditions for its preparation[63]. All three valency orbitals of the $(C_5H_5)_2M$ group in these compounds are involved in forming metal–hydrogen bonds. As a consequence, the complexes are monomeric, and are not protonated in strong acids[92].

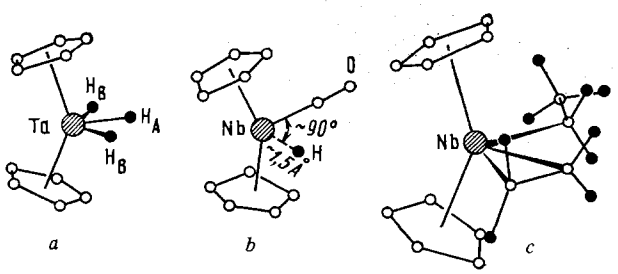
Because of the abnormally intense absorption bands ν(Ta–H) of terminal bonds it was assumed[92] that the tantalum–hydrogen bond in the trihydride is largely ionic in character. The nuclear magnetic resonance spectrum of the trihydrides in the high-field region consists of a triplet (A) and a doublet (B_2) (Table 1) with the intensity ratio 1 : 2, which corresponds to the AB_2 system of protons[92]. The spectroscopic data have recently been confirmed by structural investigations[102] (Fig.4*a*, Table 3).

Both hydrides develop a strong tendency to eliminate a hydrogen molecule[107], which is consistent with a mass-spectrometric study of the tantalum complex (the main peak corresponds to the ion $C_{10}H_{11}Ta^+$).[108]

Table 2. Parameters of e.s.r. spectra of dicyclopentadienyl hydrides of transition metals.

Compound	Solvent	g-Factor	Multiplicity	a_H, G	a_M, G	a_H^{av}, G	Ref.
$Cp_2TiH \cdot OC_4H_8$	oxolan	—	doublet	11.6	—	0.4	[18]
$Cp_2TiH \cdot PPh_3$	oxolan	1.992	doublet of doublets	10.5	—	0.41	[15, 18]
$Cp_2TiH \cdot P(n\text{-}Bu)_3$	C_6H_6	1.992	doublet of doublets	10.7*	—	0.40	[15]
Cp_2TiHCl–Li^+	C_6H_6	1.983	doublet	7.0		—	[15]
Cp_2TiHCl–Na^+	C_6H_6	1.983	doublet	9.1	—	—	[15]
Cp_2TiH_2–Li^+	oxolan	1.994	triplet of quartets	9.8	—	0.27	[56]
Cp_2TiH_2–Li^+	Et_2O	1.994	triplet of quartets	9.5	—	—	[15]
Cp_2TiH_2–Li^+	Et_2O	1.992	triplet	8	6.5	—	[55]
Cp_2TiH_2–Na^+	oxolan	1.993	multiplet	10.1	7.2	—	[15]
Cp_2TiH_2–Na^+	oxolan	1.994	multiplet	9.8	7.4	—	[56]
Cp_2TiH_2–$MgBr^+$	Et_2O	1.993	triplet	7.8**	—	0.39	[15, 101]
Cp_2NbH_2	C_6H_6	2.010	decet of triplets	11.7***	45.9	—	[52]
$Cp_2Nb(H)Bu\text{-}t$	C_6H_6	2.001	decet of doublets	11.6	68.5	—	[52]
Cp_2TaH_2	C_6H_6	2.006	octet	****	66	—	[52]
Cp_2WH *****	CH_3CN	—	—	1.9	—	—	[33]

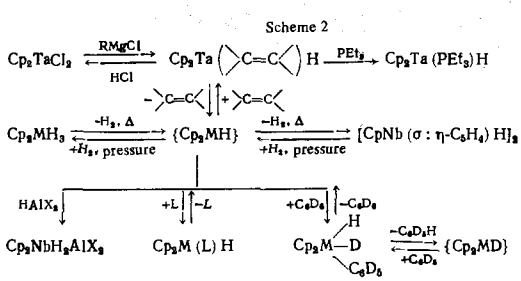
* a_D = 1.7 G.
** a_D = 2.4 G (quintet).
*** a_D < 2 G.
**** Hyperfine structure of lines due to hydrido-protons not resolved.
***** In phenanthraquinone complex.



a *b* *c*

Figure 4. Molecular structure of: *a*) $(C_5H_5)_2MH_3$ (M = Nb, Ta)[102]; *b*) $(C_5H_5)_2Nb(CO)H$;[103] *c*) $(C_5H_5)_2Nb(C_2H_4)C_2H_5$.[104]

Scheme 2



M=Nb, Ta; X=H, Et, OCH_2CH_2OMe; L= CO, PR_3, C_2H_4

Heating the niobium trihydride in the absence of a ligand leads to formation of niobocene[63]. This reaction, like the others in Scheme 2, involves intermediate formation of unstable $(C_5H_5)_2NbH$.[63,78] This explains also the hydrogen–deuterium exchange of hexadeuterobenzene with molecular hydrogen in the presence of the trihydride[63,107].

Heating the trihydrides with a trialkylphosphine, carbon monoxide, or an alkene gives complexes $(C_5H_5)_2M(H)L$, in which the lone pair of electrons occupies one of the valency orbitals (obviously $1a_1$) of the $(C_5H_5)_2M$ group[63,109]. In the niobium and tantalum complexes $(C_5H_5)_2MHL$ with L = PR_3, CO (π-accepting ligands) the chemical shift of the hydrido-protons is observed upfield relative to the initial hydrides (similarly for $(C_5(CH_3)_5)_2Z(L)H_2$), but ν(M–H) is displaced to longer wavelengths. With a π-donor ligand (ethylene) the opposite shifts are observed (Table 4).

Table 3. Structural data on dicyclopentadienyl hydrides of transition metals.

Compound	M to, A								Ref.
	$C_{C_5H_5}$	ring centre	α°	M–H_1, A	M–H_1, A	M–H_2, A	∠H_1MH_1, deg	∠H_1MH_2, deg	
Cp_2NbH_3	2.37	2.06	141	1.65	1.76	1.65	126	65	[102]
$Cp_2Nb(H)CO$	2.36	2.04	143	1.5	—	—	90	—	[103]
Cp_2TaH_3	2.39	2.07	140	1.77	1.78	1.78	125.8	63	[102]
Cp_2MoH_2	2.28	1.94	145.8	1.69	1.69	—	75.5	—	[105]
Cp_2WH_3+Cl–	2.26	1.87	148.2	—	—	—	—	—	[102]
$(Cp_2WH)_2H$+ClO_4–	—	—	145.6	—	—	1.8	—	—	[33]
$[(C_5Me_5)_2ThH_2]_2$	—	—	—	2.29	2.29	2.03	—	58	[106]

X-Ray structural analysis has shown[103] that in the $(C_5H_5)_2Nb(H)CO$ molecule the carbonyl group and presumably the hydrogen atom lie in the *yz* plane (Fig. 4b). According to n.m.r. data the structure of the $(C_5H_5)_2Nb(H)C_2H_4$ complex is closely similar to that of the ethyl complex $(C_5H_5)_2$.$Nb(C_2H_4)C_2H_5$, in which the ethylenic carbon atoms and the α-carbon atom of the ethyl group also lie in the *yz* plane[104] (Fig. 4c).

Because of the presence of a lone pair of electrons the compounds $(C_5H_5)_2M(H)L$ are Lewis bases. Thus treatment of $(C_5H_5)_2Nb(H)CO$ with hydrogen chloride at −30 °C is

stated[110] to give an unstable cationic complex $(C_5H_5)_2Nb(CO).H_2^+Cl^-$, which decomposes with the evolution of hydrogen. Donor–acceptor complexes containing metal–metal bonds have been reported to be formed by $(C_5H_5)_2Nb(H)CO$ with iron tetracarbonyl[111] and zinc tetrahydroborate[112].

Paramagnetic dicyclopentadienyl dihydrides of niobium and tantalum, isoelectronic with $[(C_5H_5)_2TiH_2]^-$, have been reported[52] (Table 2).

Table 4. Spectroscopic characteristics of complexes of dicyclopentadienyl hydrides of metals with π-acceptor and π-donor ligands.

Compound	ν(M–H), cm^{-1}	Δν(M–H), cm^{-1}	τ_{MH}, ppm	$\Delta\tau_{MH}$, ppm	Ref.
$Cp_2Nb(H)CO$	1695	−15	16.39	+2.67	[63]
$Cp_2Ta(H)CO$	1750	0	16.80	+2.62	[63]
$Cp_2Nb(H)PMe_3$	1635	−75	17.84	+4.12	[63]
$Cp_2Nb(H)PEt_3$	1650	−60	17.69	+3.97	[63]
$Cp_2Ta(H)PEt_3$	1705	−45	19.54	+6.52	[63]
$Cp_2Nb(H)(C_2H_4)$	1735	+25	12.95	−0.77	[63]
$Cp_2Ta(H)$ (Alkene)	1750–1700	0±50	—	—	[109]
$(C_5Me_5)_2ZrH_2(CO)$	—	—	8.93	+5.37	[16]
$(C_5Me_5)ZrH_2(PF_3)$	—	—	9.45	+5.89	[16]

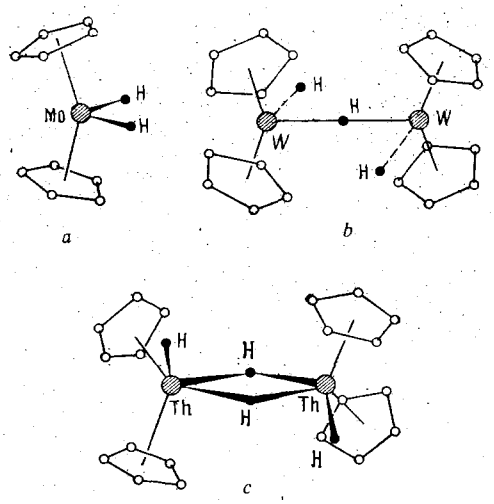


Figure 5. Molecular structure of: *a*) $(C_5H_5)_2MoH_2$;[105] *b*) $((C_5H_5)_2WH)_2H^+ClO_4^-$;[33] *c*) $[(C_5(CH_3)_5)_2ThH_2]_2$.[106]

Groups VI–VIII

According to the scheme of molecular orbitals of $(C_5H_5)_2ML_n$ in Fig. 2 the hydrides $(C_5H_5)_2MH_2$ (M = Mo, W) should possess a lone pair of electrons. In fact research shows[93–95,105,113] that these monomeric hydrides contain two equivalent terminal hydrogen atoms (Fig. 5*a*). The small HMoH angle (Table 3) is consistent with Alcock's model[86] (lone pair ~ 80% localised on *y* axis[105]). However, the structure of the protonated tungsten complex $[(C_5H_5)_2WH_3]^+Cl^-$ is closely similar to that of the niobium trihydride[102]: i.e. the central hydrogen atom is apparently situated on the *z* axis (hydrogen atoms not located).

The presence of the lone pair in the dihydrides determines their chemical behaviour. They are readily protonated by strong acids to cations $(C_5H_5)_2MH_3^+$ isoelectronic with the tantalum trihydride[62], and form donor–acceptor complexes with transition-metal carbonyls[114] and other Lewis acids (BX_3, AlX_3).[93,94,115,116] The spectroscopic characteristics of the M–H bond remain unchanged.

For tungsten a paramagnetic hydride $(C_5H_5)_2WH$ (Table 2) and a cationic hydrido-complex $((C_5H_5)_2WH)_2H^+ClO_4^-$ have also been described[33]. In the spectra of the cation ν(W–H) differs by 180 cm^{-1} and τ_{WH} by 3.9 ppm (all hydrogen atoms equivalent) from the values for the initial dihydride. X-Ray data indicate that the cation contains a linear W–H–W bridge (Table 3) (positions of hydrogen atoms estimated by analogy with the structure of the molybdenum dihydride) and terminal tungsten–hydrogen bonds[33] (Fig. 5*b*).

The rhenium and technetium monohydrides $(C_5H_5)_2MH$ contain two lone pairs, apparently occupying equivalent orbitals. However, only one orbital is protonated, which is attributed to weakening of the basic strength by acquisition of a positive charge. The ionic adduct $(C_5H_5)_2ReH_2^+Cl^-$ is completely stable, and sublimes in a vacuum at 140 °C without decomposition[64]. The two hydrogen atoms in the cation are equivalent, so that its structure is analogous to that of the isoelectronic molybdenum dihydride[105]. Adducts of the rhenium monohydride with BX_3 and with $Al(CH_3)_3$ have been described[93,115].

With Group VIII metals all valency orbitals in $(C_5H_5)_2M$ are occupied by lone electron pairs, and only formation of ions isoelectronic with the rhenium monohydride can be expected. Indeed ferrocene in strongly acid media gives a high-field ^1H n.m.r. signal corresponding to the $(C_5H_5)_2FeH^+$ ion[117], and a stable complex $(C_5H_5)_2FeH^+AlCl_4^-$ has been isolated[96].

Complete replacement by methyl groups of the hydrogen atoms in the cyclopentadienyl rings leads to significant stabilisation of the higher valency states. As an example, the titanium(IV) hydride $(C_5(CH_3)_5)_2TiH_2$ is stable at room temperature[13]; cryoscopic measurements indicate that this compound, like the zirconium derivative[16], is monomeric in benzene.

The low titanium–hydrogen and zirconium–hydrogen frequencies of terminal bonds (Table 1) indicate the instability of the latter. Indeed, equilibrium (1) is readily displaced to the left when the reaction mixture is heated above room temperature. The energy of a titanium–hydrogen bond in bispentamethylcyclopentadienyltitanium dihydride has been estimated[13] as 242.4 kJ mole^{-1}, which is comparable with those of the corresponding molybdenum–hydrogen and tungsten–hydrogen bonds (respectively 258.7 and 286.8 kJ mole^{-1}) obtained by combustion[118], or 251.4 and 305.2 kJ mole^{-1} from calorimetric measurements on the reactions of the dicyclopentadienyl dihydrides with tetrachloromethane in solution)[119].

The vacant orbital of the zirconium atom is involved in forming unstable complexes $(C_5(CH_3)_5)_2ZrH_2.L$, where L = CO, PF_3 (Table 4).[16]

Freezing-point measurements indicate that the thorium and uranium dihydrides are dimeric, which is related to the great size of the central atom[19]. The molecular structure containing terminal and bridging hydrogen atoms (thorium–hydrogen frequencies respectively 1410, 1360 and 1215, 1115 cm^{-1})[19] has been confirmed by X-ray examination[106] for $[(C_5(CH_3)_5)_2ThH_2]_2$ (Fig. 5*c* and Table 3). It is noteworthy that an *f*-element (thorium) departs from the classical geometry of $(C_5H_5)_2ML_3$: three hydrogen atoms do not lie in the single *yz* plane[106].

2. "Bismetallocene Hydrides" of Transition Metals

(a) Complexes Containing a Fulvalene Ligand

Bismetallocene hydrides containing a fulvalene (η-C_5H_4–η-C_5H_4) bridging ligand are now known for titanium, zirconium, hafnium, and molybdenum (Table 5).

Table 5. Physicochemical properties of bismetallocene hydrides of transition metals.

Compound	Prep.	ν(M–H), cm^{-1}	τ, ppm				Ref.
			C_5H_5	C_6H_5	C_5H_4	MH	
$(C_{10}H_8)(CpTiH)_2$	4a	1230	—	—	—	—	[35–37,53]
$(C_{10}H_8)(CpTiHClTiCp)$	5a	1222	—	—	—	—	[76]
$(C_{10}H_8)(CpZrH)_2$	4a	?	—	—	—	—	[38]
$(C_{10}H_8)(CpHfH)_2$	4a	?	—	—	—	—	[39]
$(C_{10}H_8)(CpMoH)_2$	4b,4d	1803	5.47	6.01	—	20.01	[54,80]
$(C_{10}H_8)(CpMoH)_2$	4b	1803	—	(6.53)	—	19.81	[51]
$(C_{10}H_8)[CpMo(H)(OH)MoCp]^+[PF_6^-]_2$	3	—	4.03	4.99; 4.30; 4.11; 3.10	—	21.15	[51,80]
$(C_{10}H_8)(CpMoH)_2H^+PF_6^-$	3	—	4.94	5.03; 5.11	—	22.22	[51]
$(C_{10}H_8)(CpMoH_2)_2$	5b	1815, 1841	—	—	—	—	[29]
$(C_{10}H_8)[CpMoH_2Mo(CO)Cp]$	5d	1805, 1820	—	—	—	18.38	[80]
$(C_{10}H_8)[CpMoH_2Mo(H)(SnR_3)Cp]$*	2b	1813, 1831	5.50; 5.64	5.50; 5.64	—	18.30(2); 17.91(1)	[29]
$[Cp(C_6H_4)NbH]_2$	4a	1650	5.11	—	5.60; 3.95	12.07	[9]
$Na_2[Cp(C_6H_4)NbH]_2$	4a	1720	—	—	—	—	[42]
$[Cp(C_5H_4)MoH]_2$	—	—	5.35; 5.32	—	5.35; 5.32	18.55; 18.66**	[51]
trans-$[Cp(C_5H_4)WH]_2$	4b	—	5.35	—	4.91; 5.36; 5.23; 6.28	20.51	[51]
cis-$[Cp(C_5H_4)WH]_2$	4b	—	5.32	—	4.81; 5.32; 6.27	20.59	[51]

* R = n-C_4H_9.
** Signals of *cis*- and *trans*-isomers.

Although no direct determination of the structure of "stable titanocene" has yet been made, infrared[37] and ^{13}C n.m.r.[8] spectroscopic data suggest the presence of bridging hydrogen atoms and a fulvalene ligand $(C_5H_5TiH)_2(C_{10}H_8)$ (Fig. 6*a*,*b*). It is consistent with X-ray data for the titanocene derivatives $(C_{10}H_8)(C_5H_5TiCl)_2$[120] and $(C_{10}H_8)(C_5H_5.TiOH)_2.C_4H_8O$[121] (Fig. 6*a*,*b*) and $(C_{10}H_8)(C_5H_5Ti(H)(H_2Al.(C_2H_5)_2)TiC_5H_5)$[79] obtained by the action of hydrogen chloride, water, and triethylaluminium respectively on $(C_{10}H_8).(C_5H_5TiH)_2$.

"Titanocene" and its derivatives $(C_{10}H_8)(C_5H_5TiX)_2$ are diamagnetic[36,120,121]. Coupling of the spins probably takes place through the fulvalene ligand, not through the bridging atoms[120]. A direct titanium–titanium bond, whose existence had been assumed[35], is obviously not formed, since for X = Cl, OH the Ti–Ti distance exceeds significantly the sum of the covalent radii (Table 6). Decreasing this distance would lead to excessive steric hindrance: in particular, with Ti–Ti = 2.7 Å the dihedral angle α (Fig. 6*a*) would be ~ 29°. Because of the presence of a single vacant orbital the complexes $(C_5H_5TiX)_2(C_{10}H_8)$ are Lewis acids, and give 1 : 1 complexes with oxolan[53,121].

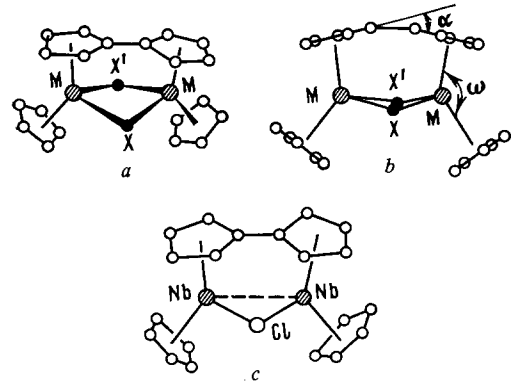


Figure 6. Molecular structure of complexes containing a fulvalene ligand: *a*) $(C_{10}H_8)(C_5H_5M(X)(X')MC_5H_5)$ (M = Ti, X = X' = Cl,[120] OH[121]); *b*) as (*a*) with (M = Mo, X = H, X' = OH[80]); *c*) $(C_{10}H_8)((C_5H_5)_2Nb_2Cl)$.[122]

Table 6. Structural characteristics of compounds of types (I) $(C_{10}H_8)(C_5H_5MX_2MC_5H_5)$ and (II) $C_5H_5M(X)(\mu\text{-}C_5H_4)_2.M(X)C_5H_5$.

Compound	M–X, Å	M–M, Å	Σ_r, Å*	M–$C_{10}H_8$, Å	M–C_5H_5, Å	M–C_6H_4, Å	ω, °	α, °	$\angle$MX^2,	Ref.
type (I)										
$C_{10}H_8)(CpTiCl_2TiCp)$	2.51	3.64	2.72	2.05	2.06	—	134.4	2.5	81.3	[120]
$(C_{10}H_8)[CpTi(OH)_2TiCp]\cdot C_4H_8O$	2.10	—	2.72	2.08	2.08	—	133.5	15.1	—	[121]
$(C_{10}H_8)(CpNbClNbCp)$	2.56	3.27	—	—	—	—	—	—	—	[122]
$(C_{10}H_8)[CpMo(H)(OH)MoCp]^+(PF_6^-)_2$	—	—	—	—	—	—	—	18	—	[80]
type (II)										
$Cp_2(\mu\text{-}C_6H_4)Ti(C_4H_8O)Cp$	—	3.37	2.72	—	—	2.19	—	—	—	[41]
$CpNb(H)(\mu\text{-}C_6H_4)_2Nb(H)Cp$	1.70	3.11	—	—	—	2.25	140.6	—	—	[9]
$[C_5H_4Si(Me)_2OSi(Me)_2C_5H_4NbH]_2Na_2[O(Et_2)_2$	1.62	3.93	—	—	—	2.31	133.7	—	—	[42]
trans- $CpW(H)(\mu\text{-}C_6H_4)W(H)Cp$	—	3.81	—	—	—	2.19	147	—	—	[123]
cis-$CpW(CH_2SiMe_3)(\mu\text{-}C_6H_4)_2W(H)Cp$	—	3.81	—	—	—	2.17	142	—	—	[123]

* Σ_r = sum of covalent radii.

"Zirconocene" and "hafnocene" are isomorphous with $(C_{10}H_8)(C_5H_5TiH)_2$, and possess similar chemical properties and physicochemical characteristics, which indicates similarity of structure between all three compounds[36,39].

Scheme 3

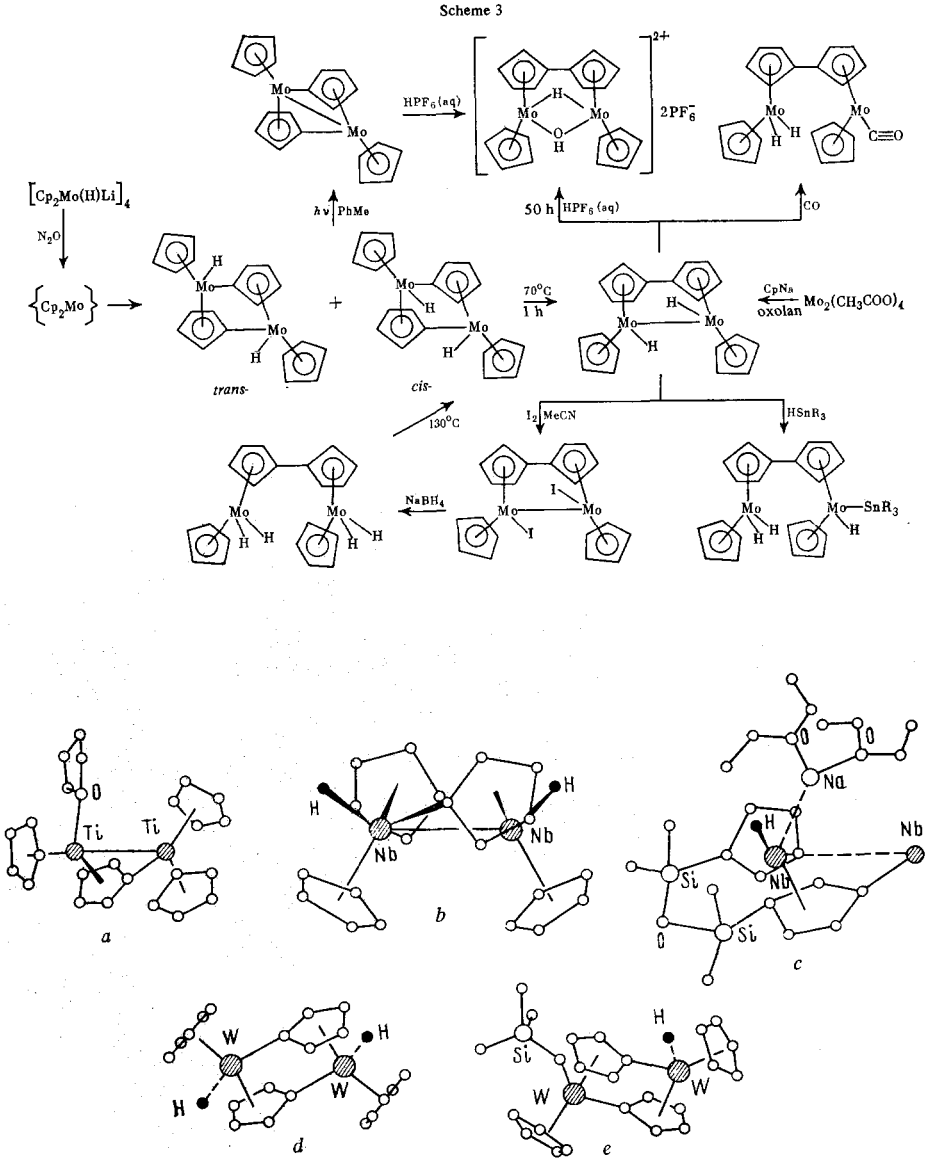


Figure 7. Molecular structure of complexes containing (σ : η-C_5H_4) bridging groups: *a*) $(C_5H_5)_2Ti(C_5H_4)Ti(C_5H_5).C_4H_8O$;[41] *b*) $C_5H_5(H)Nb(C_5H_4)_2Nb(H)C_5H_5$;[9] *c*) $Na_2(O(C_2H_5)_2)_2$. $.[(C_5H_4Si(CH_3)_2OSi(CH_3)_2C_5H_3)NbH]_2$ (fragment)[42]; *d*) *trans*-$C_5H_5(H)W(C_5H_4)_2W(H)C_5H_5$; *e*) *cis*-$C_5H_5(H)W(C_5H_4)_2W(CH_2Si(CH_3)_3)C_5H_5$.[123]

Reactions involved in the synthesis and interconversion of molybdenum hydrides containing bridging ligands η-C_5H_4–η-C_5H_4 and σ : η-C_5H_4 are shown in Scheme 3 [29,51,54,80]. Neutral fulvalene hydrides of molybdenum contain terminal molybdenum–hydrogen bonds, whereas the cationic complexes are supposed to contain Mo–H–Mo bridges, with τ_{MoH} displaced upfield (Table 5). The metal–metal bond in molybdenum(III) hydrides is readily broken to give molybdenum(IV) dihydrides. Steric hindrance in the latter is apparently eliminated by the arrangement of two metal atoms on different sides of the plane of the fulvalene ligand[54].

(b) Complexes Containing Bridging (σ : η-C_5H_4) Groups

The paramagnetic complex $(C_5H_5)_2Ti\mu$-(σ : η-C_5H_4)TiC_5H_5 gives with oxolan an equimolecular adduct[41] (Fig. 7*a*), which may contain a bridging hydrogen atom according to X-ray examination, although infrared bands corresponding to the bridging bonds have not been detected. Indirect evidence of the presence of a hydrido-atom may be provided by the high catalytic activity of this compound in the hydrogenation and isomerisation of alkenes[124]. Under hydrogen pressures of 1–10 atm it absorbs one mole of the gas to form an unstable

Table 7. Monocyclopentadienyl hydrides of transition metals isoelectronic with $(C_5H_5)_2MH_n$.

Compound	Electronic configuration	Isoelectronic analogue	Prep.	M.p., °C (decomp., °C)	ν(M–H), cm^{-1}	τ_{MH}, ppm	J_{P-H}, G	Ref.
$CpW(NO)_2H$	d^4	Cp_2NbH	5b	52	1900	7.23	—	[72]
$diarsV(CO)_3H_3$	d^2	Cp_2NbH_3	3	(135)	—	8.86	—	[126]
$CpMo(diphos)H_3$	d^2	Cp_2NbH_3	5b	—	1800, 1780	25.15	3.8	[74]
$CpMo(diphos)[Sn(n\text{-}Bu)_3]H_2$	d^2	Cp_2MoH_2	2b	—	1815	16.15	36	[74]
$CpNb(CO)(PPh_3)_2H_2$	d^2	Cp_2MoH_2	2a	—	—	—	—	[22]
$(PhMe)Mo(PPh_3)_2H_2$	d^4	Cp_2MoH_2	1a	—	1740, 1720	14.32	50.2	[17]
$CpRe(CO)(NO)H$	d^6	Cp_2WH	*	liq.	—	18.2	—	[127]
$CpMo(C_6H_6)H$	d^4	Cp_2ReH	5b	(>20)	—	11.77	—	[73]
$CpW(C_6H_6)H$	d^4	Cp_2ReH	2a, 5b	—	1822	12.2	—	[27, 60]
$CpCr(CO)_3H$	d^4	Cp_2ReH	1b, 5b	(57)	—	15.46	—	[20, 34]
$CpCr[P(OMe)_3]_3H$	d^4	Cp_2ReH	5b	(>160)	—	19.70	75	[69]
$(C_6H_6)Cr(CO)_2(SiCl_3)H$	d^4	Cp_2ReH	2b	114	—	20.5	—	[28]
$CpMo(CO)_3H$	d^4	Cp_2ReH	1a, 5b	(110)	1790	15.52	—	[14, 34]
$CpMo(CO)_2(PMe_3)H$	d^4	Cp_2ReH	*	—	—	16.59**, 15.89***	66.6**, 23.0***	[128]
$CpW(CO)_3H$	d^4	Cp_2ReH	5b	(180)	1845	17.33	—	[34]
$CpW(CO)_2(PPh_3)H$	d^4	Cp_2ReH	*	—	—	16.77**, 17.19***	66.1**, 21.4***	[128]
$CpW(CO)_2(PMe_3)H$	d^4	Cp_2ReH	*	—	1860	18.31**, 17.15***	68.3**, 24***	[129]
$CpW(CO)_2[P(OMe)_3]H$	d^4	Cp_2ReH	*	—	1860	18.55**	73**	[129]
$CpW(CO)_2[P(OMe)_3]H$	d^4	Cp_2ReH				17.66***	26***	
$CpMn(CO)_2(SiCl_3)H$	d^4	Cp_2ReH	2b	83	—	19.7	—	[28]
$CpRe(CO)_2(SiCl_2Ph)H$	d^4	Cp_2ReH	2b	—	—	—	—	[130]
$CpFe(CO)_2H$	d^6	Cp_2ReH	5b	liq.	1835	21.91	—	[34, 66]
$CpFe(CO)(SiCl_3)_2H$	d^4	Cp_2ReH	2b	—		21.6	—	[28]
$CpRu(CO)_2H$	d^6	Cp_2ReH	5b	liq.	1835	20.92	—	[34]
$CpCo(CO)(SiCl_3)H$	d^6	Cp_2ReH	2b	33		23.3	—	[28]
$CpW(CO_3H_2)^+$	d^2	$Cp_2ReH_2^+$	3	unstable	—	11.9	—	[30]
$Cp_2Mo(dppm)H^+PF_6^-$	d^2	Cp_2FeH^+	3	—	1890	17.84	36	[74]
$CpRe(C_6H_6)H^+Cl^-$	d^4	Cp_2FeH^+	3	(118)	1705	16.17	—	[131]
$CpCo(PMe_2Ph)_2H^+PF_6^-$	d^6	Cp_2FeH^+	3	—		25.2	76.5	[58]
$(C_6H_6)Mo(PPh_3)_3H^+PF_6^-$	d^4	Cp_2FeH^+	3	—	1910	10.3	72.1	[132]
$(C_6H_6)Mo(PPh_3)_3H_2^{2+}(PF_6^-)$	d^2		3	—	1880	12.3	43.5	[132]

* Substitution of carbon monoxide in carbonyl cyclopentadienyl hydrides.

** Values for *cis*-isomer.

*** Values for *trans*-isomer.

grey–green deposit, which loses hydrogen when the pressure is released. The infrared spectrum of the deposit contains a broad band at 1140 cm^{-1}, corresponding to vibration of a bridging titanium–hydrogen bond[124].

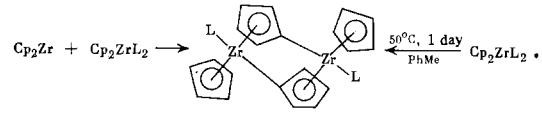
Niobocene (and obviously the isomorphous tantalocene) contain both the usual η^5-C_5H_5 groups and $\sigma:\eta$-C_5H_4 groups linking the niobium atoms in the dimer (Fig. 7*b*).[9] The length and spectrochemical characteristics of the niobium–hydrogen bond (Tables 5 and 6) are closely similar to the corresponding parameters of known transition-metal hydrides. Niobium–niobium bonds are apparently absent[9], as also in the fulvalene complex $(C_{10}H_8)(C_5H_5)_2Nb_2Cl$ (Fig. 6*c* and Table 6).[122] The corresponding hydrido-derivative has not been obtained.

Reduction of niobocene and its analogue containing Si–O–Si bridges between the rings gives the anionic complex $Na_2[C_5H_5Nb(H)(C_5H_4)]_2$.[42] On passing from the neutral compound to the dianion isoelectronic with tungstocene[123] the ν(Nb–H) frequency increases (Table 5) and the Nb–Nb distance (Fig. 7*c*, Table 6) increases, while the dihedral angle of the Nb–$C_{C_5H_4}$ bond diminishes[42].

An interesting reaction of $((C_5H_5)_2Mo(H)Li)_4$ with nitrous oxide gives a mixture of isomers $(C_5H_5MoH)_2(C_5H_4)_2$ (Table 5), which when heated or acidified form hydrido-complexes with a fulvalene ligand (Scheme 3).[80] In contrast to molybdenum, with which the fulvalene hydrides are the more stable[51], only the complexes containing bridging $(\sigma:\eta\text{-}C_5H_4)$ groups are known with tungsten (Tables 5 and 6 and Fig. 7*d*,*e*).

The above compounds are characterised by terminal metal–hydrogen bonds and exist as separable *cis*- and *trans*-isomers. The M, H, $C_{C_5H_4}$, and M′ atoms lie in the same plane[9], which is consistent with theoretical results on the nature of the bond in wedge-shaped sandwiches[85–88].

Besides hydrido-complexes bismetallocenes have been described containing μ-$(\sigma:\eta\text{-}C_5H_4)$ groups and no metal–hydrogen bond. A dark red diamagnetic complex isoelectronic with niobocene has been obtained[125]:



Hence it was assumed[125] that stable zirconocene, in contrast to titanocene, may contain $(\sigma:\eta\text{-}C_5H_4)$ groups. Formation of the corresponding molybdenum compound $C_5H_5Mo(C_5H_4)_2.MoC_5H_5$[51] is shown in Scheme 3.

3. Monocyclopentadienyl Hydrides of Transition Metals

Monocyclopentadienyl hydrides of transition metals are known, stabilised with arenes, carbon monoxide, nitric oxide, phosphines, phosphites, SiX_3, and SnX_3 (Table 7), isoelectronic with the dicyclopentadienyl hydrides $(C_5H_5)_2NbH$, $(C_5H_5)_2NbH_3$, $(C_5H_5)_2MoH_2$, $(C_5H_5)_2WH$, and $(C_5H_5)_2ReH$, and also the cation $(C_5H_5)_2FeH^+$ (Section III, 1).

Monocyclopentadienyl complexes of transition metals with ligands giving a total of four (three) electrons are formally analogous to dicyclopentadienyl hydrides of transition metals situated one (two) places to the left in the Periodic Table, but the monocyclopentadienyl hydrides possess an additional lone pair of electrons. Supplying five electrons ($C_5H_5ML_2XH_n$ complexes) changes neither the state of oxidation nor the electronic configuration of the transition metal

in comparison with $(C_5H_5)_2MH_n$. The coordination of one six-electron ligand (arene) or three two-electron π-accepting ligands yields hydrides isoelectronic with dicyclopentadienyl hydrides of immediate neighbours on the right in the Periodic Table.

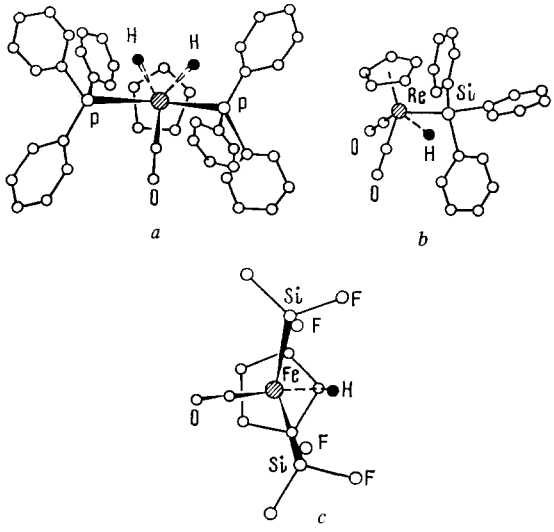


Figure 8. Molecular structure of: *a*) $C_5H_5Nb(CO)(P(C_6H_5)_3).H_2$;[22] *b*) $C_5H_5Re(CO)_2(SiCl_2C_6H_5)H$;[134] *c*) $C_5H_5Fe(CO)(Si.(CH_3)F_2)H$.[136]

It had previously been assumed that the ligand group $(CO)_3$, like an arene, should lead to the formation not only of electronic but also of structural analogues of $(C_5H_5)_2MH_n$[6,60,131]. However, X-ray examination of a series of complexes $C_5H_5M(CO)_2(SiX_3)H$ (M = Mn, Re)[133,134] and $C_5H_5Fe(CO).(SiX_3)_2H$[135,136] showed them to have a piano-stool configuration (Fig.8), in good agreement with n.m.r. results. The hydrogen atoms could not be located, and their positions were estimated from an analysis of non-bonded contacts. The length and spectroscopic characteristics of the metal–hydrogen bond (Table 7) are those usual for transition-metal hydrides.

In the case of $C_5H_5M(CO)_2(PR_3)H$ complexes *cis*- and *trans*-isomers have been obtained that differ markedly in spin–spin coupling constant (J_{P-H} ratio ~3, Table 7). Compounds containing two or more hydrogen atoms exhibit a rapid exchange of hydride protons on the n.m.r. time-scale: i.e. they are stereochemically fluximal.[17,74,126,132]

The chemical properties of monocyclopentadienyl hydrido-complexes of transition metals have been little studied, although their reactions with water, acids, halogens, and halogenated hydrocarbons are similar to those of the dicyclopentadienyl analogues. Thus $C_5H_5W(NO)_2H$ is hydrolysed by water with the evolution of hydrogen[72], whereas $C_5H_5W.(CO)_3H$ and electronic analogues of ferrocene are protonated in strong acids (Table 7).

Protonation of dinuclear complexes containing a metal–metal bond, of the types $(C_5H_5M(CO)_3)_2$ (M = Mo, W) and $(C_5H_5M(CO)_2)_2$ (M = Fe, Ru), form cationic complexes analogous to the dicyclopentadienyl complex $((C_5H_5)_2WH)_2H^+ClO_4^-$[33] and apparently containing M–H–M bridges[30]. Values of τ_{MH} in the cations $(C_5H_5M(CO)_3)_2H^+$ and $(C_5H_5M(CO)_2)_2H^+$ (some of the complexes were isolated as the fluorophosphates) are respectively 30.99, 34.8, 36.3, and 28.58 ppm for M = Mo, W, Fe, and Ru.[30]

It is interesting that protonation of the cation $(C_6H_6)M.(PR_3)_3H^+$, isoelectronic with $(C_5H_5)_2FeH^+$, gives the only known dinuclear cation $(C_6H_6)Mo(PR_3)_3H_2^{2+}$ (usually only one pair of electrons is protonated), which is attributed to the possibility of effective delocalisation of the positive charge[132].

4. Triscyclopentadienyl Hydrido-complexes of Transition Metals

Such hydrides are almost unknown. The brown complex $(C_5H_5)_3CeH$ has been reported[77], having an absorption line $\nu(Ce-H) = 2040\ cm^{-1}$. An attempt to isolate the corresponding uranium complex was unsuccessful[61]. The complex of the corresponding zirconium hydride with triethylaluminium has been isolated[137] from the $(C_5H_5)_4Zr-Al(C_2H_5)_3$ catalytic system; the link is formed by a single hydrogen bridge Zr–H–Al.

5. Transition-metal Hydrides stabilised with σ-Donor Ligands

Transition-metal hydrides stabilised with one-electron σ-donor ligands came to be studied comparatively recently. Hydrides of titanium, uranium, and thorium are known in addition to the relatively well studied zinc hydrides (configuration d^{10}) stabilised with nitrogen-containing ligands.

Reduction of diphenoxytitanium dichloride with alkali metals or sodium tetrahydroborate yields a series of hydro-complexes[138]:

$$(PhO)_2TiCl_2 \xrightarrow[oxolan]{NaBH_4} \{Ti(OPh)_2Cl(C_4H_8O)_2\}_2H$$
$$(PhO)_2TiCl_2 \xrightarrow[PhMe]{K} \{Ti(OPh)_2\}_3H$$
$$(PhO)_2TiCl_2 \xrightarrow[oxolan]{Na/tig.\ N_2} \{Ti(OPh)_2\}_3(N_2)H\ .$$

Titanium–hydrogen absorption bands have not been detected in them, but their hydride character is confirmed by the formation of chloroform on treatment with tetrachloromethane. The titanium atoms are assumed to be linked by bridging hydrogen atoms and phenoxy-groups[138].

Stable complexes $[((CH_3)_3Si)_2N]_3MH$ (M = U, Th) have been obtained[139] by boiling the corresponding chlorides with $NaN(Si(CH_3)_3)_2$ in oxolan. The hydride hydrogen originates from the solvent, as is confirmed by experiments with octadeutero-oxolan. These hydrides can be obtained also by treating the chloride with t-butyl-lithium or lithium triethylhydroborate in pentane. The metal–hydrogen bond in them has a fairly low stretching frequency, 1430 and 1480 cm^{-1} for the uranium and thorium complexes respectively[139], close to that for the corresponding terminal bond in $[(C_5(CH_3)_5)_2.ThH]_2$ (Table 1).

IV. CHEMICAL PROPERTIES OF TRANSITION-METAL CYCLOPENTADIENYL HYDRIDES

Since in the work covered above attention has been paid mainly to preparing and establishing the structure of the hydrido-complexes, their chemical properties have remained almost uninvestigated. Reactions demonstrating the presence of a metal–hydrogen bond have been mainly studied.

1. Thermal Stability and Reaction with Oxygen

Almost all cyclopentadienyl hydrides of transition metals decompose when heated, with the evolution of hydrogen and often without melting. Published data on decomposition points are given in Tables 1 and 7. The dicyclopentadienyl complexes are more stable than hydrides containing a single cyclopentadienyl group. In a series of compounds of the same type the stability increases regularly with the atomic number of the metal. As a consequence, it has proved impossible to obtain molybdenum analogues of certain tungsten complexes[30,72]. Hardly any detailed study has been made of the thermolysis of cyclopentadienyl hydrides of transition metals. Quantitative evolution of hydrido-hydrogen has been reliably determined in only a few cases (for $(C_5(CH_3)_5)MH_2$ (M = Ti, Zr, U)[13,16,19], $C_5H_5M(CO)_3H$ (M = Cr, Mo, W), and $C_5H_5Fe(CO)_2H$[3,4]). In most cases the decomposition of dicyclopentadienyl hydrides apparently involves the cyclopentadienyl ligand, yielding bridging C_5H_4 or $C_{10}H_8$ groups.

Hardly any study has been made of the action of oxygen on cyclopentadienyl hydrides of transition metals, although many publications emphasise the great sensitivity of these compounds (especially of Groups IV and V) to oxidation.

2. Reactions of Hydrido-complexes with Water and Acids

The reactivity of cyclopentadienyl hydrides of transition metals towards water and aqueous acids, involving the evolution of hydrogen, diminishes regularly on passing from left to right along the Periodic Table: whereas compounds of Group IV transition metals are hydrolysed vigorously by water, those of Group V are moderately hydrolysed, and hydrides of Groups VI–VIII metals are not in general hydrolysed. This is due to diminution in the hydride character of the metal–hydrogen bond (or negative charge on the hydrogen atom). The reactivity of the dicyclopentadienyl hydrides towards the reduction of ketones varies similarly[140]. It is interesting that the complex $C_5H_5W(NO)_2H$, isoelectronic with $(C_5H_5)_2NbH$, is hydrolysed with the evolution of hydrogen, in contrast to $(C_5H_5)_2WH_2$.[72]

The composition of the hydrolysis products was not usually studied, but formation of a hydroxyl derivative of stable titanocene by the action of a stoichiometric quantity of water has been reported[121]. Reaction with hydrogen halides (aqueous or anhydrous) generally results in replacement of a hydrido-ligand by halogen[37,76,124]. Treatment of the dicyclopentadienyl hydrides of tervalent titanium, tantalum, and zirconium with hydrogen chloride leads to oxidation of the metal with evolution of hydrogen and formation of the dichlorides $(C_5H_5)_2MCl_2$.[16,21,109]. This reaction provides a method for identifying a metal–hydrogen bond (see also subsection 3) when n.m.r. investigation is impossible, while infrared metal–hydrogen absorption bands are overlapped by other bands or even are not observed. Evolution of hydrogen deuteride on reaction with deuterium oxide or chloride is regarded as a reliable criterion[7]. Thus this method has shown the presence of a titanium–hydrogen bond in the complex $((C_5H_5)_2.TiN)_2H_3$[90,99] and in the product of the action of diphenylzinc on $(C_5H_5)_2Ti(C_6H_5)_3$.[141] The latter is assumed to contain a fulvalene ligand and two η-C_5H_4 groups linked through the zinc atom[141].

In some cases acid hydrolysis apparently involves intermediate formation of a dihydrido-complex. Thus the cations $C_5H_5M(CO)_3H_2^+$ (M = Mo, W) are formed when the monohydrido-complexes are treated with hexafluorophosphoric acid. The complex tungsten cation evolves hydrogen rapidly, and its molybdenum analogue almost instantaneously[30].

It is assumed also that $(C_5H_5)_2NbH_2(CO)^+$ is formed by the action of hydrogen chloride on the monohydrido-complex[110]:

$$Cp_2NbCl_2 \xrightarrow[2)\ NEt_3,\ CO]{1)\ NaBH_4} Cp_2Nb(H)CO \xrightarrow[-30^\circ]{HCl} \rightarrow Cp_2NbH_2(CO)^+Cl^- \xrightarrow[-H_2]{\Delta} Cp_2Nb(Cl)CO\ .$$

It is noteworthy that its action on niobocene, in contrast to titanocene[37], gives the usual $(\eta$-$C_5H_5)_2NbCl_2$.[42] A similar course is shown by other reactions of oxidative addition involving niobocene[40] and also $(C_5H_5)_2Ti(\sigma:\eta$-$C_5H_4)TiC_5H_5$.[124] These reactions may be expected to apply generally to all hydrides containing μ-$(\sigma:\eta$-$C_5H_4)$ groups, but not to complexes having a fulvalene ligand.

The action of acids on cyclopentadienyl hydrides of Groups VI–VIII transition metals gives protonated complexes, which are discussed in the appropriate subsections.

3. Reactions of Hydrido-complexes with Halogens and Halogenated Hydrocarbons

The action of halogens on the cyclopentadienyl hydrides leads to replacement of a hydrido-ligand by halogen[72], often accompanied by oxidation of the transition metal. For example, "niobocene" gives with bromine dicyclopentadienylniobium dibromide[42], and iodine acts on $(C_5H_5MoH_2)_2(C_5H_4$–$C_5H_4)$ to give the molybdenum(IV) complex $(C_5H_5MoI_2)_2(C_5H_4$–$C_5H_4)$.[29]

The formation of chloroform when a complex is treated with tetrachloromethane also provides a reliable criterion of the presence of a metal–hydrogen bond[7]. The titanium–hydrogen bond in phenoxytitanium hydrides has been demonstrated in this way[138]. In the course of the reaction hydrogen is replaced by halogen with formation of corresponding complexes. Methods of preparation of cyclopentadienyl halides have been described for the complexes $[((CH_3)_3Si)_2N]_3MH$ (M = Th, U)[139] and $C_5H_5Mo(CO)_3H$[142] with tetrachloromethane, and for $(C_5H_5)_2MH_2$ (M = Mo, W)[143] and $C_5H_5Mo(diphos).H_3$[74] with bromoform. The reactivity of $CHal_nH_{4-n}$ diminishes as n decreases, but it has been reported[7] that dichloromethane acts on $(C_5H_5)_2MH_3$ (M = Nb, Ta). Iodomethane is an extremely effective agent, in some cases enabling the content of hydrido-hydrogen to be determined quantitatively (from the evolution of methane) on reaction with $((C_5H_5)_2TiN)_2H_3$,[90] $(C_5H_5)_2Zr(H)(C_{10}H_7)Zr(C_5H_5)_2$,[21] $C_5H_5MoH(\sigma:\eta$-$C_5H_4)_2Mo(H).(C_5H_5)_2$, and $(C_5H_5)_2MoH_2$,[143] and also the corresponding iodo-derivatives to be obtained[51,143].

4. Complex Formation with Lewis Acids

Lewis acids (BX_3, AlX_3, MgX_2, $M(CO)_n$, etc.) form with the cyclopentadienyl hydrides two types of complexes—either of donor–acceptor type containing a metal–metal bond involving the lone pair of a Group VI or VII transition-metal hydride or with a hydrogen bridge—which are the subject of a detailed survey[144]. Here we note merely that the formation of equimolecular adducts having an M–M′ bond hardly changes the spectrochemical characteristics of the metal–hydrogen bond. However, the involvement of hydrogen atoms in forming bridging bonds leads to considerable shifts, in the frequency of this bond (up to 100–350 cm^{-1}) to longer wavelengths, and in τ_{MH} (up to 3–6 ppm) upfield[144].

5. Metallation of Hydrido-complexes at Metal–Hydrogen Bonds

Metallation of the metal–hydrogen bond in cyclopentadienyl hydrides has been effected by the action of butyl-lithium. The reaction with the dicyclopentadienyl dihydrides of molybdenum and tungsten gives cyclic tetramers $[(C_5H_5)_2M(H)Li]_4$ containing M–Li–M bonds.[81] Treatment of the molybdenum hydride with Grignard reagents and aluminium alkyls also results in fission of a molybdenum–hydrogen bond and formation of complexes containing bonds between molybdenum and respectively magnesium[82] and aluminium[83]. Analogous metallation by n-butyl-lithium has been described for $(C_5H_5MoH)_2(C_5H_4{-}C_5H_4)$[29] and $(C_5H_5)_2TaH_3$.[84] Apparently the metal–hydrogen bonds in the thorium and uranium complexes $[((CH_3)_3Si)_2N]_3MH$ also undergo metallation during preparation of the deuterated complexes[139]:

$$[(Me_3Si)_2N]_3ThH_2 \xrightarrow[2)\ CF_3COOD]{1)\ n\text{-}LiBu} [(Me_3Si)_2N]_3ThD\ .$$

All metallation products are strong nucleophiles, extremely sensitive to oxygen and readily hydrolysed with regeneration of the metal–hydrogen bond.

6. Reactions of Hydrido-complexes with Donor Molecules

Reaction with donor molecules may or may not involve a metal–hydrogen bond.

The presence of vacant orbitals on a transition-metal atom usually results in the formation of solvates. Stable titanocene gives an adduct with oxolan[35–37], and niobocene adducts with acetonitrile and aromatic hydrocarbons[40]. Monomeric $(C_5(CH_3)_5)_2ZrH_2$ gives unstable equimolecular complexes with carbon monoxide and phosphorus trifluoride[16]. The orbitals of Groups VI–VIII metals are filled with d-electrons, and the hydrido-complexes acquire basic properties. However, the reaction of carbon monoxide with $(C_5H_5MoH)_2(C_5H_4{-}C_5H_4)$ (Scheme 3) probably involves addition of the donor molecule to the isomer $C_5H_5MoH_2(C_5H_4{-}C_5H_4)C_5H_5Mo$ at the molybdenum(II) atom[54].

Ligand substitution not involving a metal–hydrogen bond

$$CpML_3H + L' \rightarrow CpML_2L'H + L$$

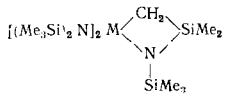
has been reported for L = CO, L′ = PR_3, $P(OR)_3$, and M = Mo, W[128] and for L = $P(OCH_3)_3$, L′ = CO, and M = Cr.[69]

A TiH_2Ti bridge undergoes homolytic fission by donor molecules (oxolan, PR_3)[15,19] (Eqn.2).

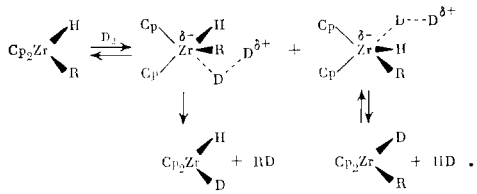
Hydrido-ligands are displaced from $(C_5H_5)_2Ti(\sigma:\eta\text{-}C_5H_4)$.$TiC_5H_5.H_2$[124] and (ArH)Mo$(P(C_6H_5)_3)_2H_2$[17] by nitrogen to form dinitrogen complexes. Carbon monoxide "displaces" a hydrogen atom from a cyclopentadienyl group in $(C_5H_5)_2ReH$ to give the cyclopentadiene complex $C_5H_5Re(CO)(C_5H_6)$.[145] Such ligands as carbon monoxide, trialkylphosphines, and alkenes displace two hydrogen atoms from $(C_5H_5)_2MH_3$ (M = Nb, Ta) (Scheme 2)[63,109]. Reaction between $((C_5H_5)_2TiN)_2H_3$ and carbon monoxide is accompanied by partial evolution of hydrogen and formation of a complex, from which $(C_5H_5)_2Ti.(CO)_2$ can be obtained by pyrolysis[99].

7. Isotope Exchange

Solid $((C_5H_5)_2TiH)_2$ exchanges protons of its cyclopentadienyl rings for deuterium in an atmosphere of the latter. Subsequent treatment with hydrogen chloride yields $(C_5D_5)_2.TiCl_2$.[57] The reaction apparently involves a hydride-transfer stage. An analogous reaction has been described for $[((CH_3)_3Si)_2N]_3MH$ (M = U, Th).[146] Formation of the completely deuterated product $[((CD_3)_3Si)_2N]_3MD$ is assumed to involve an intermediate four-membered metallobutane ring derivative



isolated on pyrolysis of the hydride[146]. Deuterium exchange in $(C_5H_5)_2Zr(H)R$ apparently proceeds via an intermediate five-coordinated complex[71]:



On contact of $C_5H_5Cr[P(OCH_3)_3]_3H$ with deuterium more than 50% of the hydrogen atoms are exchanged, presumably via a hydrogen-detachment stage and oxidative addition of deuterium[69].

Catalytic isotope exchange has been reported[63,107] between benzene and deuterium or between hexadeuterobenzene and hydrogen in the presence of $(C_5H_5)_2TaH_3$ (Scheme 2). Isotope exchange with $(C_5H_5)_2ReH$ and $(C_5H_5)_2MH_2$ (M = Mo, W) in the presence of deuterium oxide is accelerated by acids (owing to formation of protonated complexes)[34,62,64].

8. Reactions of Hydrido-complexes with Unsaturated Molecules

Alkyl complexes are formed by the action of alkenes on cyclopentadienyl hydrides of transition metals. Titanocene absorbs an equimolecular quantity of an alkene[147,148], with disappearance of the band at 1230 cm^{-1}.[148] Zirconium(IV) hydrides such as $(C_5H_5)_2ZrH_2$ and $(C_5H_5)_2Zr(H)Cl$ respectively give the complexes $(C_5H_5)_2ZrR_2$ and $(C_5H_5)_2Zr(R)Cl$[91,149]. Addition of ethylene to $(C_5H_5)_2Nb(H)(C_2H_4$[63] and of tetrafluoroethylene to $C_5H_5M(CO)_3H$ (M = Mo, W)[150] and $C_5H_5Fe(CO)_2H$[151] yields the corresponding ethyl complexes.

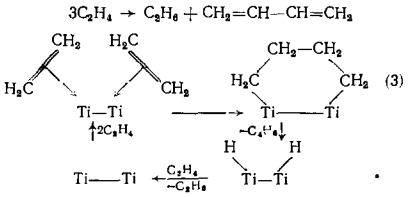
Conjugated dienes form the corresponding π-allyl complexes, as e.g. with $((C_5H_5)_2TiH)_2$[18] and $C_5H_5Mo(diphos)H_3$.[74] However, the complexes $C_5H_5M(CO)_3H$ (M = Cr, Mo, W) hydrogenate dienes selectively, and are converted into $(C_5H_5M(CO)_3)_2$.[152,153] Reaction between $(C_5H_5)_2WH_2$ and isoprene results in hydrogenation of the latter and formation of the complex $(C_5H_5)_2W(H)C_6H_5$, obviously by oxidative addition of benzene to dicyclopentadienyltungsten[154].

Dicyclopentadienylmolybdenum dihydride adds readily[155] at C:C and N:N bonds to give respectively $(C_5H_5)_2Mo(H).(CR{:}CHR)$ and $C_5H_5Mo(H)(RN.NHR)$.

9. Catalytic Activity of Hydrido-complexes

Catalytic activity is exhibited by cyclopentadienyl hydrides only of transition metals in Groups IV and V, mainly titanium and zirconium. It was reported[156] that titanocene was an effective catalyst for the hydrogenation of alkenes, but recent work has shown[15] that its activity is less by factors of 10^3–10^4 than that of systems comprising $(C_5H_5)_2TiCl_2$ with a metal alkyl. Alkenes are dimerised by titanocene in the presence of a methylhydropolysiloxane[157]. Titanocene and

$(C_5H_5)_2Ti(\sigma:\eta\text{-}C_5H_4)TiC_5H_5$ catalyse also the conversion of ethylene into butadiene, which probably involves double β-elimination:



Other hydrogenation catalysts are $(C_5H_5)_2Ti(\sigma:\eta\text{-}C_5H_4)\cdot TiC_5H_5$,[124] $((C_5H_5)_2TiN)_2H_3$,[99] and the zirconium compounds $(C_5H_5)_2ZrH_2$[91,149] and $(C_5H_5)_2Zr(H)(C_{10}H_7)Zr(C_5H_5)_2$,[21] which readily add alkenes at metal–hydrogen bonds (subsection 8).

The intermediate species $(C_5H_5)_2TiH$ (or $(C_5H_5)_2Ti(H)Cl$) is assumed to be the true catalyst, in systems based on $(C_5H_5)_2TiCl_2$ together with AlR_3, LiR, MgRX, $LiAlH_4$, or $HAl(N(C_3H_7)_2)_2$ (in non-solvating solvents), for hydrogenation[15], intramolecular cyclisation of cyclododecatriene[157], hydrometallation of alkenes[158], etc. This hypothesis is consistent with the catalytic activity of $(C_5H_5)_2TiCH_3$ after treatment with hydrogen[159]. In the case of systems containing aluminium hydrides, however, the catalytic activity of $(C_5H_5)_2TiH$ is doubtful, owing to the formation of very stable dimetal complexes having bridging hydrogen bonds[144].

Catalytic hydrogenation of ethylene on the complex $(C_5H_5)_2\cdot Nb(H)(C_2H_4)$ has been reported[63]. Blocking of the terminal hydrogen atom (by complex formation with triethylaluminium) inhibits the catalyst[160].

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Use of Chemical Lasers to Determine the Rate Constants of Reactions Between Atoms and Molecules and the Rate Constants of the Relaxation of Vibrationally Excited Molecules

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The application of chemical lasers to the determination of the rate constants of reactions and of the relaxation of vibrational excitation is discussed. The following procedures are reviewed: the measurement of the time lag of the generation with respect to the leading edge of the pulse used to initiate the reaction, the measurement of the generation decay time, the use of competing reactions to measure the rate constants of "non-laser" reactions, and also methods of measuring the relative rate constants for the population of different levels in the reaction product (the "equal amplification temperature" method, the "zero amplification temperature" method, and the "grating selection" method). 71 references.

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I. INTRODUCTION

Several methods of measuring the rate constants of reactions of atoms and radicals with molecules in the gas phase are available: spectroscopy, mass spectrometry, ESR, etc. However, the rate constants determined by different methods often show serious discrepancies, which complicate the selection of values for use in kinetic investigations. The differences in the rate constants of fast reactions of atoms and radicals with molecules are especially large. Furthermore, the range of application of these methods is often limited. Therefore the development of new experimental methods of measuring the rate constants of reactions of atoms and radicals with molecules is of great interest. A new method of measuring the rate constants of the relaxation of excited molecules would also be of great use.

The development of chemical lasers created the possibility of using the generation of radiation to measure the rate constants of the "pumping" reactions taking place in the lasers. These include, in particular, reactions such as

$$A + BC \rightarrow AB^{\dagger} + C$$

where A is an atom, BC is a molecule, and $AB^{\dagger}$ is a molecule formed in a vibrationally excited state. If the "pumping" reaction is a chain reaction the generation is determined by

several rate constants. For example,

$$Cl + H_2 \xrightarrow{k_1} HCl + H$$
$$H + Cl_2 \xrightarrow{k_2} HCl^{\dagger} + Cl .$$

The presence of several rate constants makes their determination more difficult. Furthermore, relaxation of the vibrationally excited molecules takes place in parallel with the other reactions, and this further complicates the determination of the kinetic constants k_1 and k_2. Nevertheless, as has been demonstrated experimentally, these difficulties can be overcome, and under certain conditions the kinetic constants of the reactions between atoms and molecules are relatively easily found from measurements of the oscillation parameters, with a precision at least equal to that of the more traditional methods.

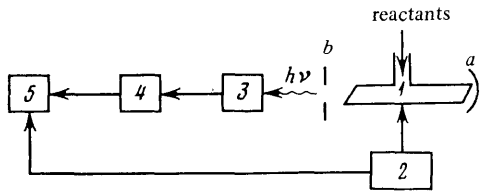


Figure 1. Block diagram of a chemical laser: *1*) laser tube, *2*) initiation system, *3*) monochromator, *4*) i.r. detector, *5*) oscillator.

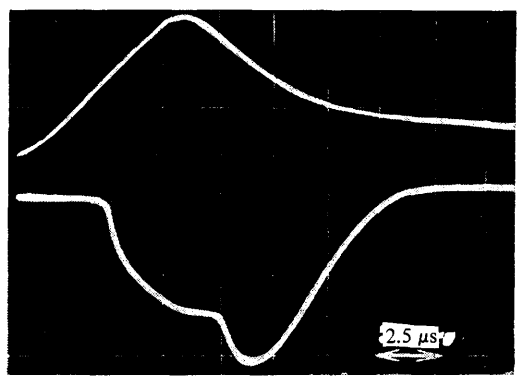


Figure 2. Oscillograms of the initiation pulse (upper trace) and the generation pulse (lower trace).

The basic principles of the determination of the kinetic and relaxation constants by using chemical lasers can be briefly illustrated as follows. The radiation from a chemical laser arises from a chemical reaction which produces excited molecules with a population inversion in different vibrationally excited states. A block diagram of the chemical laser is shown in Fig.1. The chemical reaction takes place in a cell containing the gas mixture within an optical resonator consisting of the mirrors *a* and *b* (the latter being half-silvered). The reaction in the chemical laser is initiated by atoms formed by the dissociation of molecules under the influence of a light pulse or a pulsed electrical discharge.

The length of the initiating pulse depends on the parameters of the initiating equipment used. The beginning of the initiation pulse is separated from the onset of laser generation by a time interval imposed by the need to reach the threshold concentration of the inverted population of excited molecules, which depends on the radiation losses in the resonator. The length of this time lag can be measured from oscillographic displays of the generation and initiation pulses, as shown in Fig.2.

II. DETERMINATION OF THE CONSTANTS BY MEASURING THE OSCILLATION DELAY TIME

1. Principle of the Method

By measuring the oscillation delay time t_1 and equating the concentration of population-inverted molecules at time t_1 to the threshold value needed to satisfy the self-excitation condition we can obtain an equation for the required rate constant. Allowance must be made for the radiation losses in the resonator. The experimental conditions (initiation, pressure of reactants, amount of inert diluent) are chosen so as to make the consumption of reactants and the temperature rise of the working mixture during the time lag period negligibly small.

The possibility of measuring rate constants by the oscillation delay time method was first demonstrated by Basov and coworkers[1]. Chester and Hess[2] measured the dependence of the oscillation delay time (with respect to the leading edge of the initiating light pulse) on the rate constant of the "pumping" reaction, on the intensity of the initiating light flux, on the radiation losses in the resonator, on the composition and pressure of the gas mixture, and on the relaxation processes. They considered a chemical laser operating by the reaction RF + H_2 + B (where B is an inert gas). The atomic fluorine formed by the photolysis of RF takes part in the "pumping" reaction

$$F + H_2 \xrightarrow{k_{H_2}} HF^{\dagger} + H \qquad (1)$$

giving population-inverted $HF^{\dagger}$ molecules.

The basic kinetic equations are

$$d[RF]/dt = -s(t)[RF] \qquad (2)$$
$$d[F]/dt = qs(t)[RF] - k_{H_2}[F][H_2] \qquad (3)$$
$$d[H_2]/dt = -k_{H_2}[F][H_2] \qquad (4)$$
$$d[HF]/dt = -d[H_2]/dt \qquad (5)$$

where $s(t) = \Phi \int \sigma(\lambda) I(\lambda, t) d\lambda$, Φ is the yield of the photodissociation RF, $\sigma(\lambda)$ is the molecular absorption coefficient of RF, $I(\lambda, t)$ is the local intensity of the light flux at the wavelength λ, and q is the number of F atoms formed by the dissociation of the RF molecule.

It was shown[2] that the temperature rise due to light absorption and to reaction (1) in time t_1 is negligible, and can be made even smaller by adding an inert gas to the reaction mixture. The frequency of the initiating light is chosen to lie outside the absorption bands of hydrogen and of the diluent gas. It was also shown[2] that the reactions of H, H_2, and HF with R and RF during time t_1 can be ignored, and so can also the recombination of atoms in the volume and at the walls. The process can be treated as quasi-isothermal.

In order to simplify the solution of the system of equations (2)–(5) the experimental conditions must be chosen so that the functions I and s can be expressed as

follows:

$$I(\lambda, t) = I_0(\lambda)\, t^m$$
$$s(t) = \Phi \int \sigma(\lambda)\, I_0(\lambda)\, d\lambda t^m = s_0 t^m,\ m > 0.$$

The initial conditions are $[F]_0 = [HF]_0 = 0$.

The system (2)–(5) can be transformed into

$$d[H_2]/dt = -k_{H_2}\left\{[H_2]_t - [H_2]_0 + q[RF]_0\left(1 - \exp\left(\frac{-s_0 t^{m+1}}{m+1}\right)\right)\right\}[H_2]_t\ , \qquad (6)$$

By solving Eqn.(6) we can find $[HF]_t$:

$$[HF]_t = [H_2]_0 - [H_2]_t\ .$$

Let $\Delta n(t)$ be the difference in concentration between the $HF^\dagger$ molecules in the vibrationally excited levels $(v+1)$, $(J-1)$ and v, J, corresponding to the emission of a laser line with maximum amplification:

$$\Delta n(t) = [HF_{v+1,\,J-1}]_t - [HF_{v,J}]_t\ .$$

We then have $d[\Delta n(t)]/dt = f_{H_2} d[HF]/dt - k'[M]_t \Delta n(t)$, where f_{H_2} is the difference between the probabilities of formation [by reaction (1)] of HF molecules in the upper $(v+1)$ and in the lower (v) level, and k' is the rate constant for the relaxation on M molecules.

Eqn.(6) can be integrated numerically, but alternatively the solution can simply be expanded in powers of t, retaining only the first-order terms. Since the time interval is small, deactivation occurs mainly by collisions with the initial H_2, RF, and diluent molecules, and we can assume that $[M]_t = [M]_0$. Therefore

$$\Delta n(t) \simeq \frac{f_{H_2} q k_{H_2} [RF]_0 [H_2]_0 s_0 t^{m+2}}{(m+1)(m+2)} \times \left\{1 - \frac{k_{H_2}[H_2]_0 t}{m+3} - \frac{k'[M]_0 t}{m+3} + \ldots\right\}\ , \qquad (7)$$

Oscillation begins after time t_1 (measured from the beginning of the initiating pulse), when $\Delta n(t)$ reaches the critical (threshold) value Δn_{thr}, depending on the radiation losses in the resonator:

$$\Delta n(t_1) = \Delta n_{thr}\ , \qquad (8)$$

Retaining only the lower-order term, i.e. ignoring the relaxation of the excited $HF^\dagger$ molecules, we obtain from (7) and (8) the following expression for the generation time lag, which includes the required constant k_{H_2}:

$$t_1 = \left\{\frac{(m+1)(m+2)\Delta n_{thr}}{f_{H_2} q k_{H_2} [RF]_0 [H_2]_0 s_0}\right\}^{1/(m+2)}. \qquad (9)$$

If $m = 1$ we have

$$t_1 \sim (g_0/\alpha\alpha' s_0)^{1/3} p_{tot}^{-2/3}$$

where p_{tot} is the total pressure of the mixture, α and α' are the mole fractions of H_2 and RF, and g_0 is the threshold amplification of the laser i.e. the amplification at the onset of oscillation.

The threshold amplification is related to the radiation losses in the resonator by the expression

$$(1-l)\exp(2g_0 L) = 1\ , \qquad (10)$$

where l is the loss of radiation in the resonator for a single passage of the beam, determined by the precision of the optical assembly, the reflectivity of the mirrors, the transparency of the windows in the laser tube, etc. L is the length of the optical path in the active medium.

Thus the rate constant of the "pumping" reaction can be determined, in principle, by measuring the oscillation delay time.

2. Rate Constants of the Reactions of Atoms and Radicals with Molecules

a) Reaction of F *atoms with* CH_4, HCl, *and* HBr. By using an $HF^\dagger$ laser the rate constants of the reactions of F atoms with other hydrogen-containing RH molecules can be determined from formula (9) if these reactions are used in "pumping" the laser. The equation for the "pumping" reaction (including the wanted k_{RH} constant) is

$$F + RH \xrightarrow{k_{RH}} HF^\dagger + R\ , \qquad (11)$$

Since formula (9) was obtained by ignoring the relaxation of the vibrationally excited $HF^\dagger$ molecules we must test whether the experimental conditions were correctly chosen, i.e. whether the condition $t_1 \propto p_{tot}^{-2/3}$ is obeyed when the intensity of the light flux is a linear function of time. If this expression applies we can find the ratio of the generation time lags in mixtures of H_2 + RF + B and RH + RF + B for equal partial pressure of RF and of the hydrogen donors. If $m = 1$ we have from Eqn.(9)

$$k_{RH} f_{RH}/k_{H_2} f_{H_2} = (t_1^{H_2}/t_1^{RH})^3$$

since the experimental conditions are specially chosen to make Δn_{thr}, q, $[RF]_0$, and s_0 the same in the two experiments, and $[H_2]_0 = [RH]_0$; f_{RH} is a quantity analogous to f_{H_2} and corresponds to reaction (11).

By using this method we have determined[3,4] the ratios $k_{CH_4}/k_{H_2} = 2 \pm 0.2$, $k_{HCl}/k_{H_2} = 0.25$, and $k_{HBr}/k_{H_2} = 1.3 \pm 0.2$. In the calculation we adopted the values $f_{CH_4} = 0.44$, $f_{H_2} = 0.37$, and $f_{HCl} = 0.33$ (obtained by averaging published data), and $f_{HBr} = 0.12$ (given by Jonathan and coworkers[5]).

b) The H + ClF *reaction.* The measurement of the oscillation delay time has been used to determine the rate constants of "pumping" reactions involving other atoms. Thus, the rate constant of the reaction H + ClF → $HCl^\dagger$ + F has been determined[6]. The experiment involved measuring the oscillation delay time on $HF^\dagger$ and $HCl^\dagger$ molecules in a chemical laser working on a mixture of ClF + H_2. The formation of F and Cl atoms took place by photodissociation of ClF.

The main sub-threshold processes are

$$ClF + h\nu \rightarrow Cl + F$$
$$F + H_2 \xrightarrow{k_{H_2}} HF^\dagger + H \qquad (1)$$
$$H + ClF \xrightarrow{k_{ClF}^{(1)}} HCl^\dagger + F \qquad (12)$$
$$H + ClF \xrightarrow{k_{ClF}^{(2)}} HF^\dagger + Cl\ , \qquad (13)$$

The Cl + H_2 reaction is much slower than the F + H_2, and it can be ignored in a sub-threshold process. Theoretical calculations[7,8] suggest that $k_{ClF}^{(1)} < k_{H_2}$, $k_{ClF}^{(2)} < k_{H_2}$, and $k_{ClF}^{(1)} > k_{ClF}^{(2)}$: this suggestion was confirmed by kinetic measurements[9], which gave $k_{ClF}^{(1)}/k_{ClF}^{(2)} = 6.1$, and by i.r. chemiluminescence measurements[10], which gave $k_{ClF}^{(1)}/k_{ClF}^{(2)} = 6.7 \pm 0.8$. Therefore in the pre-threshold period we can legitimately ignore the formation of $HF^\dagger$ by reaction (13) in comparison to reaction (1), and assume that the consumption

of hydrogen atoms is negligible before the onset of generation on $HCl^{\dagger}$.

By solving the equation for the change in concentration of atomic fluorine with a linearly time-dependent light flux, and by integrating the equation for the change in concentration of HF, we can arrive at the threshold concentration of population-inverted excited $HF^{\dagger}$ molecules:

$$\Delta n_{\text{thr}}^{\text{HF}^{\dagger}} = f_{\text{H}_2} \int_0^{t_{l_1}} k_{\text{H}_2} [\text{H}_2]_0 [\text{F}]_t \, dt \qquad (14)$$

where t_{l_1} is the generation time lag for the P_2 (3) transition of the HF molecules, which occurs first.

By the same procedure we can determine the threshold concentration of population-inverted excited $HCl^{\dagger}$ molecules:

$$\Delta n_{\text{thr}}^{\text{HCl}^{\dagger}} = f_{\text{ClF}} \int_0^{t_{l_2}} k_{\text{ClF}}^{(1)} [\text{ClF}]_0 [\text{H}]_t \, dt \qquad (15)$$

where f_{ClF} is a coefficient analogous to f_{H_2} corresponding to reaction (12), and t_{l_2} is the oscillation delay time for the P_2 (5) transition of the HCl molecules. Furthermore

$$\Delta n_{\text{thr}}^{\text{HF}} / \Delta n_{\text{thr}}^{\text{HCl}} = \sigma_{v,J\to v',J'}^{\text{HCl}} / \sigma_{v',J\to v',J'}^{\text{HF}}$$

where $\sigma_{\nu,\ J \to \nu',\ J'}$ is the cross-section of the initiating radiation for the given vibrational–rotational transition of the HF and HCl molecules,

$$\sigma_{v,J\to v',J'} \simeq A_{v,J\to v',J'} M^{1/2} / \nu^3$$

where $A_{\nu,\ J \to \nu',\ J'}$ is the Einstein coefficient for the transition, ν is the transition frequency, and M is the molecular weight.

From the ratio of Eqns.(14) and (15) we can obtain an expression for $k_{\text{ClF}}^{(1)}$. We calculated this constant by using Einstein coefficients taken from Refs.11 and 12, and an assumed k_{H_2} value of 2.5×10^{-11} cm^3 s^{-1}. The values $f_{\text{H}_2} = 0.36$ and $f_{\text{HCl}} = 0.31$, which describe the differences in occupancy probability of the $\nu = 2$ and $\nu = 1$ levels for HF and HCl molecules, were obtained by averaging published values for HF [13–15] and for HCl [16,17] (for the reaction $H + Cl_2 \to HCl^{\dagger} + Cl$). In this way the value $k_{\text{ClF}}^{(1)} = (3.7 \pm 0.4) \times 10^{-12}$ cm^3 s^{-1} at 300 K was obtained for the first time. The i.r. chemiluminescence method[18] had yielded only the ratio of this constant to the rate constant of the reaction $H + Cl_2 \to HCl^{\dagger} + Cl$, equal to 1.99.

c) The $OD^{\dagger} + O_3$ *reaction.* Measurements of the oscillation delay time on $CO_2^{\dagger}$ molecules in a chemical laser working on an $O_3 + D_2 + CO_2$ mixture have been used[19] to determine the rate constant of the reaction between the OD radical and O_3. The main reactions in this mixture are

$$\begin{aligned}
&O_3 + h\nu \xrightarrow{k_0(t)} O(^1D) + O_2\\
&O(^1D) + D_2 \xrightarrow{k_1} OD^{\dagger}(v) + D\\
&D + O_3 \xrightarrow{k_2} OD^{\dagger}(v) + O_2\\
&OD^{\dagger}(v) + CO_2 \xrightarrow{k_3^v} OD^{\dagger}(v-1) + CO_2^{\dagger}\\
&O(^1D) + M \xrightarrow{k_4} O(^3P) + M\\
&OD^{\dagger}(v) + O_3 \xrightarrow{k_5} \begin{cases} \to DO_2 + O_2\\ \to OD + O + O_2\\ \to D + 2O_2 \end{cases}\\
&O(^1D) + O_3 \xrightarrow{k_6} O_2 + O_2\\
&OD^{\dagger}(v) + D_2 \xrightarrow{k_7^v} OD^{\dagger}(v-1) + D_2
\end{aligned}$$

where $CO_2^{\dagger}$ is a CO_2 molecule in the (00°1) state, k_3^{ν} and k_7^{ν} are the rate constants for the reactions in the OD radical in the level ν, and $k_0(t)$ is the rate constant for the formation of $O(^1D)$ atoms from ozone under the influence of light.

3. Rate Constants of the Relaxation of Vibrational Excitation

The determination of the rate constants for the relaxation of vibrational excitation is very important in chemical kinetics, because vibrational excitation plays a key role in overcoming the activation barriers of reactions. The measurement of relaxation rate constants is especially important in the theory of chemical lasers because the intensity and duration of the generation are largely determined by relaxation processes.

The relaxation rate constants of vibrationally excited molecules can be measured, at present, by monitoring the intensity of laser-excited fluorescence at room temperature or by heating the gas mixture in a shock tube, or by the i.r. chemiluminescence method. As we shall show, the laser method (by measuring the generation time lag) can be used to determine the rate of relaxation and of transfer of vibrational excitation under appropriately chosen conditions (composition of the laser mixture, and other factors which determine the relaxation processes).

a) The $OD^{\dagger} + CO_2$, $OD^{\dagger} + D_2$ *processes.* Measurements of the oscillation delay time have shown[19] that at 300 K the rate constant of the deactivation of OD radicals ($\nu = 1$) by collisions with D_2 molecules is $k_7^1 = (3.1 \pm 0.7) \times 10^{-14}$ cm^3 s^{-1}, and the rate constant of the transfer of vibrational energy from the OD radical ($\nu = 1$) to CO_2 is $k_3^1 = (1.9 \pm 0.7) \times 10^{-12}$ cm^3 s^{-1}. The latter value is significantly higher than the value $k_3^1 = (0.5 \pm 0.25) \times 10^{-12}$ cm^3 s^{-1} obtained[20] by a similar method but without allowance for the radiation loss in the resonator. Thus failure to correct for losses in the resonator can yield low values of the rate constant.

b) The $DF^{\dagger} + CO_2$ *reaction.* The measurement of the oscillation delay time has been used[1] to determine the rate constant of the transfer of vibrational energy from the $DF^{\dagger}$ molecule to the CO_2 molecule. The time lag of the generation was measured for the (00°1 → 10°0) transition of the CO_2 molecule in a chemical laser working with an $F_2 + D_2 + CO_2$ mixture. The most important elementary processes in such a mixture are

$$\begin{aligned}
&F_2 + h\nu \xrightarrow{k_0(t)} 2F\\
&F + D_2 \xrightarrow{k_1} DF(v) + D\\
&D + F_2 \xrightarrow{k_2} DF(v) + F\\
&DF(v) + CO_2 \xrightarrow{k_3} DF(v-1) + CO_2(00°1)\\
&CO_2(00°1) + M \xrightarrow{k_4} CO_2(00°0) + M \qquad (16)\\
&DF(v) + M \xrightarrow{k_5} DF + M \qquad (17)
\end{aligned}$$

where M is any molecule in the mixture.

In the initial stages of a chemical reaction, lasting ~10^{-5} s after initiation, the processes (16) and (17) can be ignored, because the vibrationally excited states of the DF and CO_2 molecules have fairly long lifetimes. If we also ignore the time (~10^{-6} s) for the establishment of a quasi-stationary concentration of D atoms according to the equation $k_1[F][D_2] = k_2[D][F_2]$ we may characterise the formation of vibrationally excited DF and CO_2 molecules by the expressions

$$(d/dt)[DF(v)] = W(t) - k_3[DF(v)][CO_2] \qquad (18)$$

$$(\mathrm{d}/\mathrm{d}t)[\mathrm{CO_2}(00^\circ 1)] = k_3[\mathrm{DF}(v)][\mathrm{CO_2}] \cdot \quad (19)$$

The reaction rate $W(t)$ in Eqn.(18) is given by

$$W(t) = 2k_1[\mathrm{F_2}][\mathrm{D_2}]\{1 + k_1[\mathrm{D_2}]/k_2[\mathrm{F_2}]\}^{-1}\int_0^t k_0(t')\,dt' \cdot \quad (20)$$

Integration of (18) and (19) gives

$$[\mathrm{CO_2}[00^\circ 1)]_t = k_1[\mathrm{CO_2}]\int_0^t \{\exp(-k_3[\mathrm{CO_2}]t')\int_0^{t'}\exp(k_3 \times \times[\mathrm{CO_2}]t'')W(t'')\,\mathrm{d}t''\}\,\mathrm{d}t' \cdot \quad (21)$$

Laser action begins at time t_1 after the front of the light pulse. During this time the occupancy of the upper lasing level of the CO_2 molecule reaches the threshold value. If this threshold value and the reaction rate $W(t)$ are known, the rate constant for the transfer of vibrational energy (k_3) can be determined by Eqn.(21).

It is assumed that the shape of the initiating pulse can be described by the expression

$$k_0(t) = \gamma_1 t\exp(-\gamma_2 t) \quad (22)$$

where the coefficients γ_1 and γ_2 define the amplitude and the duration of the pulse. From Eqns.(20)–(22) we obtain, after integration,

$$[\mathrm{CO_2}(00^\circ 1)](t_l) = W'f(\alpha, \gamma_2, t_l)$$

where $\alpha = k_3[\mathrm{CO_2}]$, and W' is calculated by the expression

$$W' = 2k_1[\mathrm{F_2}][\mathrm{D_2}]\{1 + k_1[\mathrm{D_2}]/k_2[\mathrm{F_2}]\}^{-1}\gamma_1/\gamma_2^2 .$$

The quantity W' is the reaction rate after the end of the initiation pulse, i.e. at $t \to \infty$: it can be obtained from the expression $P = \hbar\omega_L VW'$, where P is the generated power, $\hbar\omega_L$ is the energy of the laser photon, and V is the volume of the laser tube.

Ignoring the radiation loss in the resonator we can write

$$W'f(\alpha, \gamma_2, t_l) = [\mathrm{CO_2}]\exp(-\hbar\omega(10^\circ 0)/kT).$$

Inserting into this expression experimental values of t_1, W', γ_2, and $[CO_2]$, and solving it for α, we obtain the rate constant for the transfer of vibrational energy from DF to CO_2: $(1.5 \pm 0.5) \times 10^{-12}$ cm^3 s^{-1} at 300 K. This is lower than the value obtained by other methods. For example, measurements of this constant from the laser-induced fluorescence of the DF molecules[21] and from their chemiluminescence[22] gave 6.4 ± 10^{-12} and 5×10^{-12} cm^3 s^{-1} at 350 and 300 K respectively.

The rate constant for the transfer of vibrational excitation from DF to CO_2 has been determined[23] with allowance for the loss of radiation in the optical resonator. The expression for the threshold population density of the upper lasing level of CO_2 includes a term which corrects for these losses. Allowance was made also for the time to establish quasi-stationary concentrations of F and D atoms (through the formation of fluorine atoms in the working mixture under the influence of light from the pulsed lamp). The shape of the pulse of radiation emitted by the lamp was described by the expression $k_0(t) = \gamma_1 t^3\exp(-\gamma_2 t)$, which gives a more exact time dependence of the radiation intensity than the expression $k_0(t) = \gamma_1 t\exp(-\gamma_2 t)$. The rate of the chemical reaction at the end of the light pulse was determined by comparing the characteristics of the laser working under different conditions rather than by measuring the power of the laser emission. With these improvements the rate constant for the transfer of energy from the first vibrational level of the DF molecule to the CO_2 molecule was found to be $(8.2 \pm 0.5) \times 10^{-12}$ cm^3 s^{-1}, i.e. close to the values obtained by other methods.

c) Relaxation of $HF^\dagger$ on chlorine fluorides. The oscillation delay time method has been used to measure the rate constants of the relaxation of vibrationally excited $HF^\dagger$ molecules in order to determine the role of this relaxation on the reactions of other species used in the chemical lasers. From the laser generation in $ClF_n + H_2(CH_4)$ mixtures the rate constants of the relaxation of $HF^\dagger$ molecules on various chlorine fluorides have been determined[24]. The main pre-threshold processes in these lasers are

$$ClF_n + h\nu \xrightarrow{s(t)} ClF_{n-1} + F$$

$$F + RH \xrightarrow{k_{RH}} HF(v) + R$$

$$HF(v) + RH \xrightarrow{k_{rel}^{RH}} HF + RH$$

$$HF(v) + ClF_n \xrightarrow{k_{rel}^{ClF_n}} HF + ClF_n$$

where k_{rel}^{RH} and $k_{rel}^{ClF_n}$ are the rate constants for the relaxation of HF(v) molecules on RH and ClF_n molecules respectively. The relaxation of HF(v) on HF can be ignored under these conditions, since the concentration of HF has been shown[2] to be three orders of magnitude lower than the concentration of reactants during the period preceding the achievement of the oscillation threshold.

The spectral composition of the radiation shows that $v = 2$ for the $ClF_5 + H_2(CH_4)$ and $ClF + H_2(CH_4)$ systems, i.e. that the first transition is $P_2(3)$. For the $ClF_3 + H_2(CH_4)$ system, $v = 1$, and the first transition is $P_1(6)$. Hence in the latter system the following relaxation is fast:

$$HF(v=2) + ClF_3 \rightarrow HF(v=1) + ClF_3, \quad (23)$$

The kinetic equations for the concentration of atomic fluorine and for the density Δn of population-inverted $HF^\dagger$ molecules take the form

$$\mathrm{d}[F]/\mathrm{d}t = s(t)[ClF_n]_0 - k_{RH}[F][RH]_0 \quad (24)$$

$$\mathrm{d}(\Delta n)/\mathrm{d}t = f_{RH}k_{RH}[F][RH]_0 - k\Delta n \quad (25)$$

where $s(t) = s_0 t\exp(-t/t_{max})$, t_{max} is the time at which $s(t)$ reaches a maximum, and

$$k = k_{rel}^{RH}[RH]_0 + k_{rel}^{ClF_n}[ClF_n]_0.$$

In order to determine the relaxation rate constants we must choose conditions such that the pressure of chlorine fluoride is higher than that of RH, since the constants k_{RH} and k_{rel}^{RH} are quite large [according to Hancock and Green[25], $k_{rel}^{H_2} = 0.7 \times 10^{-12}$ cm^3 s^{-1} for HF ($v = 1$)]. Solving the system of equations (24), (25) for the conditions

$$(k_{RH} + k_{rel}^{RH})[RH]_0 \ll k_{rel}^{ClF_n}[ClF_n]_0;\ 1/t_{max} \ll k_{rel}^{ClF_n}[ClF_n]_0$$

gives

$$\Delta n(t) = s_0\frac{f_{RH}k_{RH}}{2k^3}[(kt)^2 - 2kt + 2 - 2e^{-kt}], \quad (26)$$

The generation time lags with respect to the leading edge of the initiating pulse were measured for exit mirrors made of Ge and CaF_2 (t_1' and t_1'' respectively). Since $g_0 \propto \Delta n$, by using the experimental time lags t_1' and t_1'' for two different mirrors but identical compositions of the reactant mixture we can obtain from Eqn.(10)

$$g_0''/g_0' = \Delta n(t_1'')/\Delta n(t_1') = \lg(1 - l'')/\lg(1 - l') = C \quad (27)$$

where l' and l'' characterise the radiative losses in the resonator with Ge and CaF_2 exit mirrors respectively. By combining (26) and (27) we obtain an equation for k. The constant C can be calculated[2] from the condition $C = (t_1''/t_1')^3 \cong$

3 for low pressures. To study the relaxation on ClF_3 molecules the system of equations (24), (25) must be supplemented by an equation describing the population of the first level as a result of the relaxation of the second level during process (23).

Table 1. Relaxation rate constants (10^{12} k_{rel}, cm^3 s^{-1}) of the vibrational excitation at 300 K, obtained by measurements of the time lag (I) and of the luminescence decay (II).

Process	I	II
$OD(v=1)+CO_2 \rightarrow OD(v=0)+CO_2$	1.9±0.7 [19]	—
$OD(v=1)+D_2 \rightarrow OD(v=0)+D_2$	0.031±0.007 [19]	—
$DF(v=1)+CO_2 \rightarrow DF(v=0)+CO_2$	8.2±0.5 [23]	6.4* [21]; 5 [22]
$HF(v=2)+ClF_5 \rightarrow HF(v=1)+ClF_5$	5.1±1.7 [24]	—
$HF(v=1)+ClF_5 \rightarrow HF(v=0)+ClF_5$		
$HF(v=2)+ClF \rightarrow HF(v=1)+ClF$	0.16±0.03 [24]	0.02** [26]
$HF(v=1)+ClF \rightarrow HF(v=0)+ClF$		
$HF(v=1)+ClF_3 \rightarrow HF(v=0)+ClF_3$	5.6±1.7 [24]	3.4 [27]

*At 350 K.
**For the second process.

Numerical values of the relaxation rate constants are given in Table 1. The k_{rel} values are combined constants for the relaxation of the second and first level for ClF_5 and ClF, and of the first level for ClF_3. These values agree in order of magnitude with the relaxation rate constants calculated from luminescence quenching data[26,27].

d) The $HCl^+ + HCl$ *relaxation.* Gorshkov and coworkers[28] measured the rate constant of the exchange reaction

$$HCl(v=m)+HCl(v=n) \rightarrow HCl(v=m-1)+HCl(v=n+1)$$

by comparing calculated and measured time dependences of the amplification in an HCl chemical laser. The apparatus consisted of two chemical lasers initiated by flash photolysis and working on an $H_2 + Cl_2$ mixture, mounted on a common optical axis, and operated in the oscillator regime and as an amplifier respectively. The reaction in the oscillator (with formation of a laser pulse) was started at a known time after the beginning of photolysis in the amplifier. The amplification of the oscillator output was determined in a series of experiments with increasing time intervals between the pulses in the amplifier and the oscillator. A computer programme based on the accepted model of the ($H_2 + Cl_2$) laser was used to calculate the time dependence of the population inversion and of the amplification for a single vibrational–rotational transition of the HCl molecule. A comparison of the experimental results with those of the computer model gave the probable range of values for the rate constant of the relaxation of HCl^+ by ν–ν exchange.

III. DETERMINATION OF THE KINETIC CONSTANTS BY MEASURING THE OSCILLATION DECAY TIME

The measurement of the rate constant of the "pumping" reaction from the shape of the laser pulse depends on the fact that the relaxation of the lasing molecules, as well as several other processes, can be ignored under certain experimental conditions (low pressure, short and weak initiation reaction). In this case the decay of the laser signal is exponential, with an exponent depending only on time, on the rate constant of the "pumping" reaction, and on the initial concentration of the molecules taking part in that reaction.

1. Principle of the Method

The first reported measurement[29] of the rate constant of a "pumping" reaction from the shape of the laser pulse was aimed at determining the rate constants of the reactions of atomic fluorine with hydrogen, methane, and hydrogen chloride molecules. A more detailed description of the method appears in Ref.30, where an $NF_3 + H_2(D_2)$ laser is used to determine the rate constants of the reactions of atomic fluorine with hydrogen and deuterium molecules. The main processes in the working mixture of such a laser are:

$$NF_3 \xrightarrow{k_1} F + NF_2 \text{ (initiation)}$$

$$F + H_2 \xrightarrow{k^n_{H_2}} HF(v=n) + H \quad (1)$$

$$HF(v=n) + HF(v=m) \underset{}{\overset{k_2}{\rightleftarrows}} HF(v=n-1) + HF(v=m+1) \quad (28)$$

$$HF(v=n) + H_2(v=m) \underset{}{\overset{k_3}{\rightleftarrows}} HF(v=n-1) + H_2(v=m+1) \quad (29)$$

$$H_2(v=n) + H_2(v=m) \underset{}{\overset{k_4}{\rightleftarrows}} H_2(v=n-1) + H_2(v=m+1) \quad (30)$$

$$HF(v=n) + M \xrightarrow{k_5} HF(v=n-1) + M \quad (31)$$

$$H_2(v=n) + M \xrightarrow{k_6} H_2(v=n-1) + M \quad (32)$$

$$HF(v=n) \xrightarrow{k_7} HF(v=n-1) + h\nu_{n,n-1} \quad (33)$$

$$HF(v=n) + h\nu_{n,n-1} \rightleftarrows HF(v=n-1) + 2h\nu_{n,n-1} \text{ (stimulated emission)}.$$

In this scheme (1) is the "pumping" reaction, (28), (29), and (30) describe vibrational–vibrational energy exchange (for seven HF levels and three H_2 levels), (31) and (32) are vibrational–translational energy exchange processes, and (33) is the spontaneous emission from HF^+.

Difficulties in this method arise from the influence of a large number of elementary processes on the rate of excitation of the vibrational levels of the HF molecules, which determines the power of the oscillation. If the rates of these processes are comparable, it is not easy to extract information on any particular elementary act from the time dependence of the laser power. Therefore the constants can be determined by the "oscillation decay" method only if the parameters of the system are chosen so that the elementary act of interest plays a predominant role among all the other possible elementary acts.

Numerical calculations[30] for the $NF_3 + H_2$ system have shown that such a regime can be realised at low pressures of the $NF_3 + H_2$ mixture ($\leq$10 mmHg) and by using a weak initiation of the reaction ($[F]_0 \leq 10^{14}$ cm^{-3}). The calculations took account of reactions (1) and (28)–(33). They led to the conclusion that under certain conditions the main contribution to the excitation of the vibrational levels of HF comes from the reaction $F + H_2 \rightarrow HF(\nu = n) + H$. The contributions from other processes are at least two orders of magnitude lower (Fig.3).

By examining the material balance equations for the density of photons in the resonator and for the occupancy of the vibrational levels of HF we can show that in the quasi-stationary approximation the power of the laser radiation (in the absence of relaxation processes) is proportional to the rate of "pumping" by the reaction $F + H_2 \rightarrow HF^+ + H$. The balance equations which allow for the chemical pumping and

for the stimulated emission are

$$dn_v/dt = \alpha_v W(t) - B_{v,v-1}\Delta_{v,v-1}\rho_{v,v-1} + B_{v+1,v}\Delta_{v+1,v}\rho_{v+1,v}$$

$$d\rho_{v,v-1}/dt = B_{v,v-1}\Delta_{v,v-1}\rho_{v,v-1} - \rho_{v,v-1}/\tau_p$$

where n_ν is the population density of the vibrational level ν, $\rho_{\nu,\nu-1}$ is the density of photons in the resonator, α_ν is the probability of forming a molecule in the level ν by an elementary reaction act, $B_{\nu,\nu-1}$ is the Einstein coefficient for the stimulated emission by the transition $\nu \to \nu - 1$, τ_p is the lifetime of a photon in the resonator, $\Delta_{\nu,\nu-1}$ is the difference in population density between the levels ν and $\nu - 1$, and $W(t)$ is the reaction rate, i.e.

$$W(t) = k_{H_2}[F][H_2], \qquad (34)$$

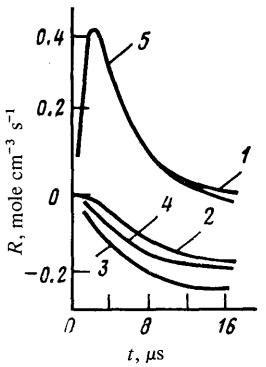


Figure 3. Rate of excitation R_i of the HF vibrational levels in the i-th process as a function of time t: *1*) $10^5 R_1$, *2*) $10^8 R_{28}$, *3*) $10^7 R_{29}$, *4*) $10^8 R_{31}$, *5*) 10^5 d[HF($\nu = 2$)]/dt.

The suggestion that laser action takes place in one vibrational–rotational transition of each band ($\nu \to \nu - 1$) does not materially affect these conclusions[30].

The power density of the radiation emerging from the resonator is

$$P = \sum_v \frac{\rho_{v,v-1}}{\tau_p}\hbar\omega_{v,v-1}.$$

For the scheme involving four equidistant levels in the quasi-stationary approximation ($d\rho_{\nu,\nu-1}/dt = d\Delta_{\nu,\nu-1}/dt = 0$) we can write

$$P = \frac{1}{2}\hbar\omega_L W(t)(3\alpha_3 + \alpha_2 - \alpha_1 - 3\alpha_0) \qquad (35)$$

where $\hbar\omega_L$ is the energy of the laser photon.

Since the concentration of fluorine atoms $[F]_0$ created by the initiating pulse is small in comparison with the initial concentration of hydrogen molecules $[H_2]_0$ we can put $[H_2]_t = [H_2]_0$. Then,

$$[F]_t = [F]_0 \exp(-k_{H_2}[H_2]_0 t), \qquad (36)$$

In the derivation of Eqn.(36) the initiating pulse was assumed to be shorter than the characteristic time of the chemical reaction. This assumption is valid under the chosen experimental conditions. From (34) and (36) we arrive at

$$\ln P(t) \sim k_{H_2}[H_2]_0 t.$$

Thus, having determined τ (the time constant of the decay of the laser pulse), and knowing $[H_2]_0$, we can calculate the rate constant:

$$k_{H_2} = 1/\tau[H_2]_0.$$

The heating of the gas by elastic collisions of electrons and heavy particles can be shown to be negligible[31]. The heating effect of the chemical reaction on the gas mixture is estimated to be less than 1 K. Heating through the relaxation of the vibrational energy of the molecules excited by the discharge becomes appreciable (at low pressures) during the later stages of the process, when the chemical reaction has gone to completion. We can therefore assume that the reaction takes place isothermally at the wall temperature of the reaction vessel.

The k_{H_2} and k_{D_2} constants have been measured[30] at 195 and 295 K. The k_{H_2} value for 295 K was close to the recommended[32] value $k_{H_2} = 2.5 \times 10^{-11}$ cm^3 s^{-1}. On the other hand the value $k_{H_2} = 6.3 \times 10^{-11}$ cm^3 s^{-1}, given in Ref.29 for room temperature, is too high, possibly because some of the fluorine atoms taking part in the reaction F + H_2 had an excess of energy, acquired during the photo-initiation. Under the chosen experimental conditions[29] the thermalisation time of the "hot" fluorine atoms could have been comparable to the time of the chemical reaction.

The decay of laser action for reactions initiated by an electric discharge has been used to determine the rate constants of reactions between fluorine atoms and a series of organic and of inorganic molecules[33]. However, the experimental conditions were not optimised for the measurement of rate constants, and the results may be in error by a factor of 1.5–3.

2. Comparison of the Rate Constants of the Reactions of Fluorine Atoms Determined by Different Methods

Rate constants determined from measurements of the delay of time agree satisfactorily with those calculated from the decay of laser oscillation[3]. Measurements of the oscillation decay time in conjunction with initiation by an electric discharge have been used to determine the rate constants of the reactions of fluorine atoms with hydrogen, methane, and hydrogen chloride molecules. By measuring the generation time lag (with photo-initiation) the ratios k_{CH_4}/k_{H_2} and k_{HCl}/k_{H_2} have been determined. The results are summarised in Table 2, from which we note that in spite of the different methods of initiation the agreement between the various results is generally good.

For comparison Table 2 also gives the rate constants obtained by other methods. For the k_{H_2}, k_{CH_4}, and k_{HCl} constants, which have been measured in many laboratories, we have adopted the values recommended in recent review articles[32,34]. It is evident from Table 2 that the rate constants determined by laser methods are fully consistent with those obtained by other methods.

Thus, in spite of the many assumptions necessarily made in the laser methods of determining kinetic constants (neglect of the relaxation of the population-inverted molecules, constancy of reactant concentrations, and failure to allow for the slower reactions), the reaction rate constants measured by these methods are as precise as those measured by other methods.

IV. THE COMPETING REACTION METHOD OF MEASURING THE RATE CONSTANTS OF REACTIONS IN CHEMICAL LASERS

The main weakness of the above laser methods of determining the kinetic constants of reactions between atoms and molecules is their severely limited range of application (to "pumping" reactions only). The scope of the method was broadened very substantially by our development[43] of a variant based on the standard kinetic method of using competing reactions. A substance whose molecules can interact with the atoms involved in the "pumping" reaction is introduced into the active medium of the laser. As a result, the atoms are contributing to two reactions in parallel within the chemical laser: 1) the "pumping" reaction, leading to laser action, and 2) the competing reaction, which suppresses the rate of the "pumping" reaction by lowering the concentration of the participating atoms. This leads to an increase in the oscillation delay time, and to a decrease in the decay time constant of the laser action. By measuring these characteristic times in the presence and in the absence of the competing reaction we can determine its rate constant.

Table 2. Comparison of the rate constants for F + X reactions determined by different methods at 300 K.

X	$10^{11}k_X$, cm^3 s^{-1}	k_X/k_{H_2}	Method
H_2	2.5	—	I [32]
H_2	2.4±0.1	—	II [30]
H_2	2.2±0.4	—	II [3]
D_2	2.12±0.10	0.86	II [30]
D_2	—	0.56	III [15]
D_2	—	0.62	IV [35]
D_2	—	0.61	V [36]
D_2	—	0.52	VI [37]
D_2	2.14	0.59	VII [38]
CH_4	8	—	I [32]
CH_4	7.2±1.2	—	I [34]
CH_4	4.6±0.7	2.1	II [3]
CH_4	—	2±0.2	VIII [3]
HCl	1.3±0.3	—	I [34]
HCl	0.7±0.2	0.3	II [3]
HCl	—	0.25	VIII [3]
HBr	—	0.65*	VIII** [4]
HBr	—	0.87±0.14*	IX [5]
HBr	—	0.68*	IX [39]
Cl_2	12.5±1.2	—	VIII [3]
Cl_2	11±3	—	VI [40]
Cl_2	16±5	—	VI [41]
Br_2	16±3	—	VIII [4]
Br_2	31±9	—	VI [41]

Notes. The k_X values for X = O_2 + O_2 and X = O_2 + N_2, determined by measuring the time lag[4] and by ESR respectively[42], are (1.0 ± 0.3) × 10^{-32} and (1.4 ± 0.4) × 10^{-32} cm^6 s^{-1}. Methods: I) recommended value, II) measurement of decay time, III) chemical laser, IV) competing reactions, V) calculated, VI) mass spectrometric, VII) ESR, VIII) measurement of delay time, IX) i.r. chemiluminescence.

*Value of k_{HBr}/k_{CH_4}.

**Assuming k_{CH_4}/k_{H_2} = 2 (after Ref.3).

The application of the competing reaction method in chemical lasers has substantially increased the range of reactions whose rate constants can be measured by laser methods. By using competing reactions we can measure the rate constants of a large number of reactions which do not give rise to laser emission. The combined method has been applied in a number of reactions between fluorine atoms and various molecules.

1. Application of the Method in Measurements of the Oscillation Delay Time

The competing reaction method was first used in conjunction with measurements of the delay time to determine the rate constant of the F + Cl_2 reaction[3], by measuring the generation time lag in H_2 + RF + He and H_2 + RF + Cl_2 + He mixtures.

The main processes in the H_2 + RF + Cl_2 + He mixture are

$$RF + h\nu \rightarrow R + F$$

$$F + H_2 \xrightarrow{k_{H_2}} HF^\dagger + H \qquad (1)$$

$$F + Cl_2 \xrightarrow{k_{Cl_2}} ClF + Cl\,. \qquad (37)$$

The Cl + H_2 reaction can be ignored, because its rate is much lower than the rates of reactions (1) and (37).

By solving the equation for the time dependence of the concentration of atomic fluorine (assuming a linear time dependence of the initiating light flux and constant reactant concentrations) we can find the threshold concentration of population-inverted excited $HF^\dagger$ molecules:

$$\Delta n_{thr} = f_{H_2} \int_0^{t_3} k_{H_2}[H_2]_0[F]_t\,dt\,.$$

The delay times of laser action by the $P_2(3)$ transition of the $HF^\dagger$ molecule were measured in H_2 + RF + Cl_2 + He and H_2 + RF + He mixtures (t_{l_1} and t_{l_2} respectively). Under these conditions $\Delta n_{thr\,1} = \Delta n_{thr\,2}$. Hence we can obtain a transcendental equation for determining k_{Cl_2}.

The same method was used[4] to determine the rate constants of the reactions

$$F + Br_2 \xrightarrow{k_{Br_2}} FBr + Br$$

$$F + O_2 + O_2 \xrightarrow{k_{O_2}} FO_2 + O_2\,,$$

2. Application of the Method in Measurements of the Oscillation Decay Time

a) Principle of the method. The oscillation decay time is measured for the $HF^\dagger$ molecules of a chemical laser operating on a mixture of RF + H_2 + X + He, where X is a molecule for which we wish to determine the time constant of the reaction with atomic fluorine (k_X).[43] In this laser reaction (1) is the "pumping" reaction. In the presence of the X molecules, which react with fluorine atoms, reaction (1) competes with the following reaction:

$$F + X \xrightarrow{k_X} \text{products}\,. \qquad (38)$$

Reaction (38) lowers the rate of reaction (1) and shortens the time constant of the decay of the laser action. Since at low pressures and for short and weak initiating pulses the oscillation strength is proportional[30] to the rate of reaction (1), and therefore to the concentration of atomic fluorine, the decay of the signal in this case is described by an exponential function with the exponent

$$-(k_{H_2}[H_2]_0 + k_X[X]_0)t$$

where $[H_2]_0$ and $[X]_0$ are the initial concentrations of hydrogen molecules and of the additive respectively. By

measuring the time constant of the decay of the laser signal (τ), and knowing $[H_2]_0$ and $[X]_0$, we can calculate k_X:

$$k_X = 1/\tau[X]_0 - k_{H_2}[H_2]_0/[X]_0.$$

The rate constant of the reference reaction (k_{H_2}) is accurately known. If necessary, other chemical laser "pumping" reactions can be used as the reference reaction.

This method was first used[3] to determine the rate constant of the reaction $F + Cl_2 \xrightarrow{k_{Cl_2}} FCl + Cl$, in conjunction with the following "pumping" reactions:

$$F + CH_4 \rightarrow CH_3 + HF^\dagger$$
$$F + HCl \rightarrow HF^\dagger + Cl.$$

The constant $k_{Cl_2} = (6.2 \pm 3.1) \times 10^{-11}$ cm^3 s^{-1} at 300 K was obtained.

b) Use of the method to measure the rate constants of the reactions of fluorine atoms with organic molecules containing multiple bonds. The determination of these constants is complicated by the simultaneous presence of two reactions: the removal of an F atom with formation of HF and the addition of an F atom at the multiple bond. The addition reaction does not lead to the formation of $HF^\dagger$ molecules with a population inversion. The removal reaction may cause inversion [for example, $F + C_2H_4$, $F + C_3H_6$, $F + iso\text{-}C_4H_8$, $F + (CH_3)_2CO$], or it may produce HF molecules without population inversion (for example, in the $F + C_6H_6$ and $F + CH_3CN$ reactions).

Table 3. Rate constants of F + M reactions (where M is a molecule containing multiple bonds) at 300 K.

M	$10^{10}\,k_{tot}$, cm^3 s^{-1}	k_{rem}/k_{add}	$10^{10}\,k_{rem}$, cm^3 s^{-1}	$10^{10}\,k_{add}$, cm^3 s^{-1}	Method***
C_2H_4	1.4±0.4 [43]	0.43 [46]	0.4* [45]	1.0* [45]	I
C_2H_4	—	—	0.4 [39]	1.5** [49,50]	—
C_3H_6	1.9±0.4 [45]	1.0 [47]	1.0* [45]	1.0* [45]	II
iso-C4H8	2.7±0.5 [45]	1.2 [47]	1.5* [45]	1.2* [45]	II
$(CH_3)_2CO$	3.2±0.8 [44]	—	1.3 [39]	1.9 [44]	I
CH_3CN	0.52±0.13 [44]	—	0.15 [39]	0.37 [44]	I
C_6H_6	1.3±0.4 [43]	—	0.8 [39]	0.5 [43]	I
C_6H_6	2.7±0.9** [48]	—	—	—	III

*Calculated by using the k_{rem}/k_{add} ratio given in Refs. 46 and 47.

**At 283 K.

***The following methods were used to determine the total interaction constant k_{tot}: I) measurement of the oscillation decay time in conjunction with a competing reaction, II) measurement of the oscillation decay time, III) radio-gas chromatography.

However, even if laser action takes place with the HF molecules, it can be so weak as to make the rate constant of the reaction impossible to measure otherwise than by the competing reaction method. This situation exists, for example, in the reactions $F + C_2H_4$ and $F + (CH_3)_2CO$, and therefore the rate constants of these reactions were determined by the present method by arranging for these reactions to compete with the pumping reaction $F + H_2$. The same method was used to determine the rate constants of the reactions $F + C_6H_6$ and $F + CH_3CN$, since in these systems oscillation does not take place on HF. The rate constants of the reactions $F + C_3H_6$ and $F + iso\text{-}C_4H_8$ were measured in the usual way by using the formula $k_{RH} = 1/\tau[RH]_0$, where $RH = C_3H_6$ or $iso\text{-}C_4H_8$, since in these systems adequate laser action on the HF molecules was obtained[45]. The measured rate constants are listed in Table 3.

The main disadvantage of applying this method of measuring rate constants to molecules with multiple bonds is that the relative contributions of the addition and removal reactions cannot be distinguished, since the measurement gives the sum of the rate constants of these reactions. However, by using existing data on the ratios of these constants[46,47] and on the rate constants of the removal reactions calculated from i.r. chemiluminescence measurements[39] we can arrive at the separate rate constants of the removal reaction (k_{rem}) and of the addition reaction (k_{add}) for these molecules (Table 3). It is clear from Table 3 that the agreement between constants determined by the laser method[45], the luminescence method[39], and the radio-gas chromatography method[48–50] is satisfactory.

Of course, if the method is applied to molecules in which the addition reaction cannot take place these complications disappear, and the constants can be determined directly. The method is suitable also for other classes of molecules. The laser method in the competing reaction variant can be applied to any atom able to undergo a reaction in which excited molecules showing a population inversion are formed.

V. METHODS OF MEASURING THE RELATIVE RATE CONSTANTS FOR THE POPULATION OF DIFFERENT LEVELS IN THE REACTION PRODUCT

Measurements of the occupancy of different vibrational levels in the molecules of reaction products can be relevant in various applications of chemical kinetics. The use of chemical lasers can offer quantitative information on the population N_v of the vibrational levels of reaction products and on the relative rate constants k_v for the formation of the product in different vibrational states.

1. The "Equal Amplification Temperature" Method

The "equal amplification temperature" method allows the ratio of the rate constants k_v/k_{v-1} for the $v \rightarrow v-1$ transition, which has the maximum amplification, to be measured directly. The method was first proposed[51] for the $F + H_2$ and $F + CH_4$ reactions. By careful temperature control in chemical lasers operating with $UF_6 + H_2(D_2)$ and $UF_6 + CH_4(CD_4)$ mixtures, and using photo-initiation, conditions giving two vibrational–rotational transitions simultaneously and with the same amplification were obtained. The ratio N_v/N_{v-1} of the occupancies of the states taking part in the first transition at the generation threshold was determined. This ratio can be identified with the ratio k_v/k_{v-1} if vibrational deactivation can be ignored. Addition of a known amount of inert diluent is sufficient to bring about a rapid rotational equilibrium[52]. Under these conditions the rotational temperature of the system is close to the initial temperature of the laser mixture, which is determined by the external application of heat to the laser tube. The self-heating of the mixture as a result of the laser reaction is negligible.

The time lag between the beginning of the $P_2(4)$ and of the $P_2(3)$ transition of the HF molecule in the $UF_6 + H_2$ system was found to decrease as the temperature of the laser tube was increased, the intensity of the $P_2(3)$ transition

decreasing while that of the $P_2(4)$ transition increased. The temperature corresponding to equal time lags (and amplifications) for the $P_2(3)$ and $P_2(4)$ transitions was found. This temperature was termed the "equal amplification temperature" for the $P_2(3)$ and $P_2(4)$ transitions.

According to Patel[53], the relative amplification $\alpha_v(J)$ of the transition ($v \to v-1$, $J-1 \to J$) is

$$\alpha_v(J) = \text{const}\ \frac{JN_{v-1}}{kT_n^{1/2}T_{\text{rot}}}\left[\frac{N_v}{N_{v-1}}B_v \exp\left(\frac{-B_vJ(J-1)}{kT_{\text{rot}}}\right) - B_{v-1}\exp\left(\frac{-B_{v-1}J(J+1)}{kT_{\text{rot}}}\right)\right] \quad (39)$$

where k is Boltzmann's constant, B_v is the rotational constant of the vibrational level v, T_n is the translational temperature, and T_{rot} is the rotational temperature (with $T_n = T_{\text{rot}}$ in the present case). When the two transitions $P_v(J)$ and $P_v(J+1)$ have equal amplifications, i.e. $\alpha_v(J) = \alpha_v(J+1)$, the ratio N_v/N_{v-1} can be obtained from the previous equation:

$$\frac{N_v}{N_{v-1}} = \frac{B_{v-1}}{B_v} \times \times \frac{J\exp[-B_{v-1}J(J+1)/(kT_{\text{rot}})] - (J+1)\exp[-B_{v-1}(J+1)(J+2)/(kT_{\text{rot}})]}{J\exp[-B_vJ(J-1)/(kT_{\text{rot}})] - (J+1)\exp[-B_vJ(J+1)/(kT_{\text{rot}})]} \quad (40)$$

where T_{rot} is the equal amplification temperature. As was stated above, $N_v/N_{v-1} = k_v/k_{v-1}$.

The method has been used to obtain the ratios k_2/k_1 for the reaction F + H_2,[51] k_3/k_2 for the reaction F + D_2,[51] k_3/k_2 for the reaction F + CCl_3D,[54] and k_4/k_3 for the reaction F + HI.[55]

Berry and Pimentel[56] have modified Eqn.(40) in order to allow for vibrational–rotational interaction, which had been previously ignored. They also examined the effect of pressure on the shape (width) of the line and on the amplification, and they extrapolated their experimental results to low pressures. At the equal amplification temperature they measured the following ratios of the rate constants for the population of the levels in the HCl molecules produced by the light-induced removal of HCl from dichloroethylene: k_3/k_2 for the 1,1 isomer and k_2/k_1 for the *cis*- and *trans*-1,2 isomers.

The "equal amplification temperature" method gives only the k_v/k_{v-1} ratio: for the other ratios it can only give upper limits, since when the oscillation threshold is reached these transitions are affected by the previous laser emission. The method has been improved[57] by using a "tandem" chemical laser with two laser tubes in the same resonator simultaneously initiated by flash photolysis. In this case the ratio of the rate constants could be measured even for transitions which do not give maximum amplification. For the photodehydrochlorination of dichloro-ethylene the k_3/k_2 and k_2/k_1 ratios of the HCl molecules were obtained for the 1,1 isomer and for the *cis*-1,2 isomer.

Molina and Pimentel[58] have described another improvement of the "equal amplification temperature" method, involving the inclusion of a diffraction grating in the optical resonator. This allows previous selection of the vibrational–rotational transitions, and hence it allows the measurement of different k_v/k_{v-1} ratios (not only those corresponding to transitions with maximum amplification). The method was used to measure the k_1/k_0 ratio for the light-induced removal of HCl from 1,1-dichloro-ethylene. The agreement with the results obtained by other methods for the ratio of the rate constants was satisfactory[58].

The drawback of using a diffraction grating in the "equal amplification temperature" method is that only the ratios of constants for transitions with relatively high amplification can be measured, since the radiation losses in the resonator are rather high. This disadvantage can be overcome by combining the tandem laser configuration and the diffraction grating, as in the "zero amplification temperature" method[58].

2. The "Zero Amplification Temperature" Method

The method[58] relies on the fact that the relative amplification of the lines in the P and R branches has different dependences on J and T. If $N_v/N_{v-1} < 1$, a single transition in the P branch will have a positive amplification over a range of temperature, but on raising the temperature the amplification will change sign. On the other hand, if $N_v/N_{v-1} > 1$, the transition in the R branch will have positive amplification at certain temperatures but the amplification will become negative as the temperature is lowered. At almost any ratio of the level occupancies (not too close to unity) there will be transitions in the P and R branches with zero amplification at accessible temperatures. The temperature at which the amplification of the transition changes from positive to negative has been termed the "zero amplification temperature".

The apparatus includes two laser tubes within a single resonator (tandem scheme). The resonator consists of a mirror and a diffraction grating in the Littrow configuration, which allows operation of the laser only on one (chosen) transition. The "leading" reaction in one tube should have enough amplification to emit radiation from this transition without assistance from the "subsidiary" reaction in the second tube, for which we wish to measure the ratio of the rate constants. If the "subsidiary" reaction gives positive amplification for the transition being studied, the time lag will be shorter than in the absence of the "subsidiary" reaction. Conversely, if the "subsidiary" reaction gives negative amplification the time lag increases. By varying the temperature of the "subsidiary" reaction we can determine the "zero amplification temperature" of this reaction. The occupancy ratio can then be found from the "zero amplification" equation, obtained by equating to zero the amplification expression [Eqn.(39)]:

$$\frac{N_v}{N_{v-1}} = \frac{B_{v-1}}{B_v}\exp\left\{\frac{hc}{kT_{za}}[B_vJ(J\mp1) - B_{v-1}J(J\pm1)]\right\}$$

where the upper sign refers to the transition $P_v \to v-1$. $[(J-1) \to J]$ and the lower sign refers to the transition $R_v \to v-1[J \to (J-1)]$; T_{za} is the zero amplification temperature.

The "zero amplification temperature" method usefully complements the "equal amplification temperature" method. Each has a number of advantages, depending on the properties of the reaction of interest. The "zero amplification temperature" method needs a suitable "leading" reaction, offering stable generation of the required transitions with an amplification sufficient to overcome the relatively large losses in the resonator. If such a reaction can be found, the results are more readily interpretable than those of the "equal amplification temperature" method. In particular, there is no need to correct for vibrational–rotational interaction or for the pressure dependence of the line shape.

3. Determination of the Temperature Dependence of the Ratio of Constants

Though the chemiluminescence and molecular beam methods give qualitative information on the effect of temperature on the reactions of interest, a quantitative interpretation is very difficult. Chemical lasers offer a far more satisfactory

method of studying the temperature dependence of the distribution of the reaction product over the vibrational states. In the laser experiments the temperature is the primary experimental variable, and the conditions are chosen so as to ensure precisely defined rotational and translational temperatures.

Both the "equal amplification temperature" and the "zero amplification temperature" method can be used to obtain temperature dependences. The former can be used because the transitions with maximum amplification vary with temperature. For example[59], in the F + D_2 removal reaction the "equal amplification temperature" for the $P_3(4)-P_3(5)$ transitions ($v = 3 \rightarrow 2$ band) of the product DF is 301 K, for the $P_3(5)-P_3(6)$ transitions it is 567 K, and for the $P_3(3)-P_3(4)$ transitions it lies below 153 K. This gives the temperature dependence of the k_3/k_2 ratio.

The "zero amplification temperature" method can be used to obtain temperature dependence because transitions with different J values have different "zero amplification temperatures". Transitions for which the "zero amplification temperature" is accessible must be chosen. The method has been used[59] to determine the temperature dependence of the ratios of constants k_v/k_{v-1} for the F + H_2 removal reaction. For the $v = 3 \rightarrow 2$ band the measurements were carried out on transitions of the P branch, since in this case $k_3/k_2 < 1$. The "leading" reaction was F + HBr → HF^+ + Br. For the $v = 2 \rightarrow 1$ band the measurements were made on the R branch because in this case $k_2/k_1 > 1$. This time the "leading" reaction was F + CH_4 → HF^+ + CH_3. By using a combination of the "equal amplification temperature" and the "zero amplification temperature" method the temperature dependence of the ratios of constants k_3/k_2 and k_2/k_1 was obtained[59]. The combined method has also been used[60] to study the effect of rotation on the distribution of vibrational energy in the F + H_2 reaction at different temperatures by using hydrogen enriched with the *para*-modification.

The temperature dependence of the ratio of constants has been obtained[61] also for another class of reactions: insertion–removal between NH and fluoromethanes. Though the flash photolysis of HN_3 in the presence of fluorinated methanes and argon does not yield laser generation, it was possible to measure the k_v/k_{v-1} ratios as a function of temperature for CF_4, CF_3H, and CF_2H_2 by using the "zero amplification temperature" method in a tandem scheme.

4. The "Diffraction Grating Selection" Method

This method relies on a frequency-selective resonator consisting of a mirror and a diffraction grating in the Littrow configuration. As mentioned above this resonator allows the laser to be operated on a single, chosen, vibrational–rotational transition. Measurements of the relative time lags of the various transitions can be used to characterise the vibrational population inversion in terms of the optical amplification coefficients[15]. According to Patel[62],

$$\alpha_{v,J\rightarrow v',J'} = (\text{const})\, \nu \Delta\nu_D^{-1} |R_{v,J\rightarrow v',J'}|^2 \left(\frac{N_{v,J}}{g_J} - \frac{N_{v',J'}}{g_{J'}}\right) H^P_{v,J\rightarrow v',J'} \quad (41)$$

where ν is the frequency of the transition and $\Delta\nu_D$ is its Doppler width. Furthermore,

$$|R_{v,J\rightarrow v',J'}|^2 = |M_{v\rightarrow v'}|^2 S_{J'} F_{v,J\rightarrow v',J'}$$

where $M_{v \rightarrow v'}$ is a matrix element of the transition, $S_{J'} \equiv J'$ for transitions of the P branch and $S_{J'} \equiv J' + 1$ for transitions of the R branch, $F_{v,\ J\rightarrow v',\ J'}$ is the vibrational–rotational interaction factor, and $H^P_{v,\ J\rightarrow v',\ J'}$ is a correction factor for the line width, depending on the pressure, which includes the Doppler and the collision broadening. For a rotationally thermalised sample we have

$$N_{v,J} = N_v g_J \exp[-\Delta E^v_{\text{rot}}(J)/kT]/Q^v_{\text{rot}}$$

where $\Delta E^v_{\text{rot}}(J)$ is the rotational energy of the state (v, J), and Q^v_{rot} is the rotational distribution function.

The amplification coefficients were calculated from published data on the transition frequencies, rotational energies, vibrational matrix elements, vibrational–rotational interaction factors, and collision line widths. For the amplification to be positive, the population inversion ($N_{v,\ J}/g_J - N_{v',\ J'}/g_{J'}$) in Eqn.(41) must be positive. This requirement leads to the following conditions: for a transition in the R branch

$$\frac{N_v}{N_{v-1}} \geqslant \frac{Q^v_{\text{rot}}}{Q^{v-1}_{\text{rot}}} \exp\left(\frac{\Delta E^v_{\text{rot}}(J+1) - \Delta E^{v-1}_{\text{rot}}(J)}{kT}\right)$$

and for a transition in the P branch

$$\frac{N_v}{N_{v-1}} \geqslant \frac{Q^v_{\text{rot}}}{Q^{v-1}_{\text{rot}}} \exp\left(\frac{\Delta E^v_{\text{rot}}(J-1) - \Delta E^{v-1}_{\text{rot}}(J)}{kT}\right),$$

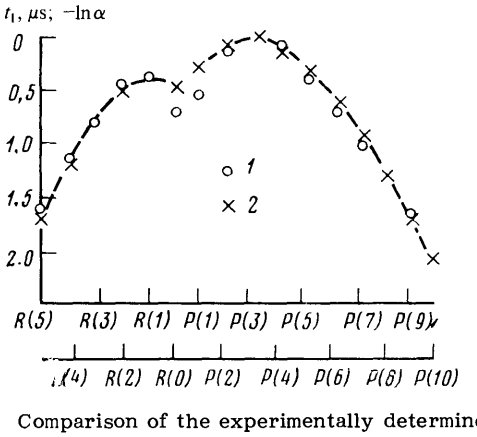


Figure 4. Comparison of the experimentally determined delay time t_1 (*1*) and the calculated values ln α (*2*) for $v = 2 \rightarrow 1$ transitions in HF. The amplification coefficients were calculated by Eqn.(41) for $N_2/N_1 = 3.35$ (without allowing for the factor $H^P_{v,\ J\rightarrow v',\ J'}$). The −ln α values for the $P_2(3)$ and $P_2(8)$ transitions were fitted to the measured delay times by using the expression $\alpha = \exp(-at_1)$. Introducing the pressure correction into Eqn.(41) improves the agreement for $N_2/N_1 = 3.45$ and the correspondence between the $R_2(0)$ and $P_2(1)$ transitions, which have anomalously high collision line widths.

Thus we can obtain the lower limits for $N_v/N_{v-1} = k_v/k_{v-1}$ by suitably choosing the experimental conditions (no relaxation effects, rotational equilibrium, constant temperature during the laser action). Furthermore these quantities can be determined by comparing experimentally measured time lags with calculations by the empirical equation $\alpha = \exp(-at_1)$, where a is an empirical constant.

The agreement between experimental and calculated values of t_1 is optimised by varying N_v/N_{v-1} in Eqn.(41). The procedure is illustrated in Fig.4 for the transitions of the

$v = 2 \rightarrow 1$ band of the HF molecule formed in the reaction $F + H_2$. In this way the k_v/k_{v-1} ratios have been determined for the reactions $F + H_2$, $F + D_2$, F + HD, and F + DH.[15] The results are given in Table 4. For comparison the Table also gives some values of k_v/k_{v-1} obtained by i.r. chemiluminescence and corrected (for the first time) for (v, v) and (v, R, T) energy transfer. The v–v exchange for HF → HF and HF → H_2 and the v–R, T exchange with HF, H_2, F, Ar, CF_3I, and N_2H_4 have been calculated[63]. It was shown that for the $F + H_2$ reaction the initial N_2/N_1 ratios (equal to k_2/k_1) should be greater than those measured at time t_1. The ratio N_3/N_2 is almost insensitive to the energy exchange processes, whereas N_1/N_0 is extremely sensitive and very difficult to determine.

Table 4. k_v/k_{v-1} ratio for the HF (DF) molecules formed by removal reactions at 300 K.

Reaction	k_4/k_3	k_3/k_2	k_2/k_1	k_1/k_0	Ref.
$F+H_2 \rightarrow HF+H$	—	0.63±0.04 (0,62)*	3.40±0.10 (3,8)*	5.2±0.4 (>10)*	[15]
»	—	0.48±0.01 (0,45)*	3.3	—	[59]
»	—	0.58±0.12**	3.6±0.2 **	—	[5]
»	—	0.53±0.1**	3.4±0.7 **	—	[12]
»	—	0.56±0.06**	3.4±0.3**	—	[64]
$F+D_2 \rightarrow DF+D$	0.4±0.2 **	1.80±0.10	2.35±0.10	2.3±0.2	[15]
»	—	1.6	—	—	[51]
»	—	1.5±0.1	—	—	[59]
»	0.66±0.13 **	1.5±0.3**	2.3**	—	[12]
$F+HD \rightarrow HF+D$	—	0.15±0.05 ***	3.1±0.2	5.2±0.4	[15]
$F+DH \rightarrow DF+H$	0.3±0,2***	1.60±0.10	2.25±0.10	2.2±0.2	[15]

*Including energy exchange correction[63].

**Measured by i.r. chemiluminescence: all other values obtained by a chemical laser method.

***Estimated from the intensity of the laser bands in the free oscillation regime.

The "diffraction grating selection" method can be used to study some isotope effects[15]. Obviously,

$$\alpha_{v,J\rightarrow v'jJ'} = N_{\text{tot}}\,\alpha'_{v,J\rightarrow v',J'}$$

where N_{tot} is the total number of HF molecules and α′ is the amplification coefficient per molecule.

If the reactant concentrations in the F + H_2 and F + HD systems are chosen so as to give identical amplification coefficients for the same transitions (as shown by the equality of the time lags) we can write

$$k_{F+H_2}[H_2]_0\,\alpha'_{F+H_2} = k^{HF}_{F+HD}[HD]_0\,\alpha'_{F+HD}$$

for equal concentrations of atomic fluorine in the two experiments and $[F] \ll [H_2]_0$, $[HD]_0$; k^{HF}_{F+DF} is the rate constant of the reaction $F + HD \rightarrow HF^{\dagger} + D$. These experiments gave $k^{HF}_{F+HD}/k_{F+H_2} = 0.38 \pm 0.03$ at 300 K, and $k^{DF}_{F+HD}/k_{F+D_2} = 0.50 \pm 0.03$, where k^{DF}_{F+DH} is the rate constant of the reaction $F + DH \rightarrow DF^{\dagger} + H$.

By combining these results with the kinetic isotope effect $k_{F+H_2}/k_{F+D_2} = 1.79 \pm 0.10$ at 300 K (obtained by measuring the full emission intensity in the free generation regime) we can calculate the intramolecular kinetic isotope effect $k^{HF}_{F+HD}/k^{DF}_{F+HD} = 1.4 \pm 0.1$ at 300 K.

The "grating selection" method has been used to study the distribution of vibrational energy in the HCl molecules formed by flash photolysis of different chloro-ethylenes[65]. Since vibrational relaxation was negligible under the conditions of those experiments we can write $N_v/N_{v-1} = k_v/k_{v-1}$. The results are shown in Table 5. For comparison the k_v/k_{v-1} values obtained by the "equal amplification temperature method" in several forms are also shown in the Table.

Table 5. k_v/k_{v-1} ratios for HCl molecules formed by photoremoval from M molecules at 300 K.

M	k_4/k_3	k_3/k_2	k_2/k_1	k_1/k_0	Method
$CH_2=CHCl$	0.78±0.01	0.91±0.01	0.90±0.02	0.86±0.03	I
$CH_2=CDCl$	0.86	1.05	0.91	0.81	I
$CH_2=CCl_2$	0.83±0.02	1.02±0.03	0.97±0.01	0.75±0.03	I
$CH_2=CCl_2$	—	0.87±0.02	—	—	II
$CH_2=CCl_2$	—	—	1.08±0.03	—	III
$CH_2=CCl_2$	—	1.06	1.07	0.78	IV
Cis-CHCl=CHCl	—	0.72	0.83	0.79	I
	—	—	0.81±0.02	—	II
	—	0.71±0.03	0.76±0.02	—	III
Trans-CHCl=CHCl	—	0.62	0.65	0.69	I
	—	—	0.70±0.02	—	II
$CHCl=CCl_2$	—	0.72	0.74	0.69	I

Notes. Methods: I) diffraction grating selection[65], II) equal amplification temperature[56], III) and IV) equal amplification temperature with a tandem arrangement[57] or a diffraction grating[58].

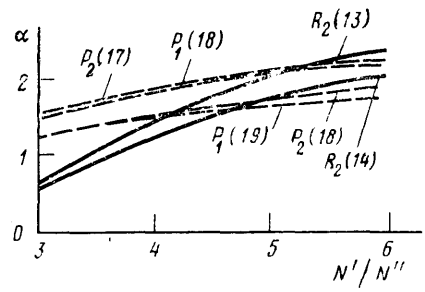


Figure 5. Relative amplification coefficients α as a function of the population inversion N'/N'' for some rotational transitions of the $A \rightarrow X$ (0, 0) band of the CN radical, calculated by assuming rotational and spin-orbit equilibrium of the CN* radical ($A^2\Pi_i$ at 300 K).

The frequency-selective resonator has been used also[66] to determine the ratio of the populations of the upper and the lower level of a laser working on an electronic transition of the CN radical formed by flash photolysis of methyl isocyanide. The relative optical amplification coefficients for the laser transitions in this case were calculated from the expression

$$\alpha = \text{const}\cdot S_{J'}\left(\frac{N'}{N''}\,\frac{\exp(-E'_{\text{rot}}/kT)}{Q'_{\text{rot}}} - \frac{\exp(-E''_{\text{rot}}/kT)}{Q''_{\text{rot}}}\right)\left(\frac{N'}{N''}+1\right)^{-1} \quad (42)$$

where $S_{J'}$ is the intensity of the rotational line, and the primes ′ and ″ refer respectively to the upper ($A^2\Pi_i$, $v' = 0$)

and the lower ($X^2\Sigma^+$, $v''=0$) laser level. The relative amplification coefficients are shown in Fig.5 as a function of the population inversion for several transitions of the $A \rightarrow X$ (0, 0) band of the CN radical. The intersections of these lines give the lower limits of the ratio N'/N''. For example, the transition R_2 (13) begins to emit before the transition P_1 (18), and therefore it has a greater amplification. This gives $N'/N'' > 5.1$. By comparing the curves for different transitions we see that $N'/N'' \cong k'/k'' > 5.3$, where k' and k'' are the rate constants of the processes which populate the upper and the lower level respectively. Similar calculations of the population ratio of the upper and the lower level can be made without a selective resonator for a laser working in the free generation regime, but in this case Eqn.(42) is applied only to the transition with maximum amplification. In this way the ratios $N'/N'' \cong k'/k''$ have been obtained for the populations of the upper ($A^2\Pi_{3/2}$, $v'=0$) and the lower ($X^2\Sigma^+$, $v''=0$) level of the CN radical formed by flash photolysis of CH_3NC, CF_3CN, HCN, C_2F_5CN, $(CN)_2$, and BrCN.[67]

The method has been used also to determine the population ratio of the upper and the lower level in HF and HCl molecules formed by insertion–removal reactions between $O(^1D)$ and fluorinated and chlorinated methanes[68–70]. The results are shown in Table 6.

Table 6. Estimates of the population ratios $N_v/N_{v-1} = k_v/k_{v-1}$ from the maximum amplification transitions for $O(^1D)$ + M addition–removal reactions.

M	Emitting molecule	v	k_v/k_{v-1}
CHF_3	HF	2	0.8 [68]
CH_3F	HF	1	0.35 [68]
$CHCl_3$	HCl	1	0.50 [69]
CH_3Cl	HCl	1	0.61 [69]
$CHCl_2F$	HF	2	0.8 [70]
$CHCl_2F$	HCl	1	0.5 [70]
$CHClF_2$	HF	2	0.8 [70]

The "grating selection" method was applied[71] in the determination of the relative population of levels in the HF molecule formed by the insertion–removal reaction $O(^3P)$ + fluoro-ethanes. The result was $N_1/N_0 \cong k_1/k_0 = 0.52 \pm 0.02$ for C_2H_3F and $N_1/N_0 \cong k_1/k_0 = 0.61 \pm 0.04$ for *cis* and *trans*-1,2-$C_2H_2F_2$ and C_2HF_3.

Thus the laser generation produced by chemical reactions in a resonator can yield important information on the rate of elementary processes in the reaction medium. Laser methods can be used to measure the rate constants of the reactions of atoms and radicals with molecules, the rates of transfer and relaxation of vibrational excitation, and the rate constants for the formation of the reaction product in different energy states. The use of competing reactions widens the scope of the laser methods and allows the rate constants of processes which are not true "laser" reactions to be determined. Thus the method has adequate generality. In spite of the many assumptions made in the oscillation delay time and oscillation decay methods, rate constants can be determined to a precision comparable to that of other methods. However, no other method is comparable to the laser methods for determining the state of vibrationally excited products.

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Electronic Spectroscopy of Charge-transfer Complexes as a Method for the Investigation of Intramolecular Interactions in Organic and Organoelemental Compounds

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The application of electronic absorption and emission spectroscopy of intermolecular donor-acceptor complexes (charge-transfer complexes) in the study of intramolecular effects of substituents in organic and organoelemental compounds is considered.

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I. INTRODUCTION

When donor (D) and acceptor (A) molecules interact with partial transfer of electron density, a donor–acceptor complex [a charge-transfer complex (CTC)] is formed:

$$D+A \rightarrow [D^{\delta+}A^{\delta-}]. \quad (1)$$

The theory of the CTC and their role in physical and chemical processes have already been considered[1-10], but virtually no systematic account has been given of data concerning the application of the electronic spectra of intermolecular CTC to the study of intramolecular interactions in donor and acceptor molecules, particularly in the case of organoelemental donors.

According to Eqn.(1), the appearance of fractional charges in D and A is accompanied by a redistribution of electron density in the molecules. However, for the ground state (GS) of weak π,π and π,σ complexes (which will be the subject of subsequent discussion) such redistribution is slight as a consequence of the small charge transfer from the donor to the acceptor[1,3]. In the ground states of the remaining complexes the contribution of the valence (donor–acceptor) interactions is not decisive in the overall balance of the intermolecular forces (see, for example, Foster[6]). When the complex undergoes a transition to an excited state, the electronic configurations of the species comprising the complex are altered even in the case of weak D–A bonds and the degree of charge transfer from D to A increases sharply. On the basis of the Mulliken theory[3], one can therefore speak of a new energetic state of the components of the complex—the charge-transfer state (CTS). In particular, the parameters of the electronic spectra of weak CTC contain information about this state. It is shown below that the intramolecular interactions in the ground and charge-transfer states as a rule do not differ in principle but many fine effects in the CTS are manifested more distinctly. Therefore the excited state of the CTC constitutes a convenient model for the investigation of a wide variety of problems associated with the distribution of electron density in the CTC components.

The main studies of recent years, devoted to the intramolecular interactions in the molecules of π-donors (derivatives of benzene, naphthalene, certain heterocyclic compounds, etc.) using the electronic spectroscopy of weak CTC, are analysed in this review. Particular attention is devoted to organoelemental π-donors.

II. ELECTRONIC ABSORPTION SPECTRA OF CHARGE-TRANSFER COMPLEXES

1. Principles of the Application of the Spectroscopy of Charge-Transfer Complexes in the Study of Intramolecular Interactions

The charge-transfer frequency ν_{CT} (the parameter which is most readily determined experimentally and is proportional to the energy of the transition with charge transfer) and the intensity of the charge-transfer band in the electronic absorption spectra of the CTC can be used to investigate the nature of the distribution of electron density in the donor molecules[3]. Fig.1 presents the energy diagram for a weak CTC, from which it follows directly that the energy of the electron transition with charge transfer is defined by the equality

$$h\nu_{CT} = W_E - W_N = W_E - \Delta H = I_D - E_A + E_C + R_E - W_N \quad (2)$$

where W_E and W_N are the energies of the excited and ground states of the CTC respectively, $W_N = \Delta H$ is the enthalpy of formation of the CTC (for weak complexes, $|\Delta H| < 10$ kcal mol^{-1}), I_D the "adiabatic" ionisation potential of the donor molecule, equal to the energy of the electronic transition from the lowest vibrational level of the ground state of the neutral molecule to the lowest vibrational level of the ion D^+, E_A the "adiabatic" electron affinity of the acceptor A, E_C the Coulombic energy whose evolution stabilises the complex in the excited state, and R_E the energy of the destabilisation of the excited complex due to the contribution of the structure D...A, the interaction in which is of the van der Waals type. The contribution of this structure to the ground state of the CTC is decisive[3], the system being stabilised by the "charge transfer energy" R_N.

The quantitative relation between the energy of the charge-transfer transition $h\nu_{CT}$, the ionisation potential of the donor I_D, and the electron affinity of the acceptor E_A is[1]

$$h\nu_{CT} = I_D - (E_A - E_C + W_0) + (\beta_0^2 + \beta_1^2)/[I_D - (E_A - E_C + W_0)], \quad (3)$$

where W_0 is the sum of the terms characterising the van der Waals interaction in the ground state, $\beta_0 = H_{01} - W_0 S$ and $\beta_1 = H_{01} - W_1 S$ are matrix elements with $H_{01} = \int \psi_0 H \psi_1 d\tau$ and $S = \int \psi_0 \psi_1 d\tau$, ψ_0 and ψ_1 being the wave functions of the structures D...O and D^+A^- respectively.

A parabolic relation between $h\nu_{CT}$ and I_D has been obtained for weak complexes of the π,π and π,σ types involving a series of isotypical donors and a constant acceptor[1]:

$$h\nu_{CT}=I_D-C_1+C_2/(I_D-C_1) \quad , \qquad (4)$$

where C_1 and C_2 are constants whose significance is clear from a comparison of Eqns.(3) and (4). For donors with ionisation potentials in the range $7 < I_D < 9$ eV, Eqn.(3) can be satisfactorily approximated by the linear relation[11]

$$h\nu_{CT}=aI_D+b \quad , \qquad (5)$$

where a and b are constants. For CTC between π-donors and iodine, $a = 0.87$ and $b = 0.36$.[1]

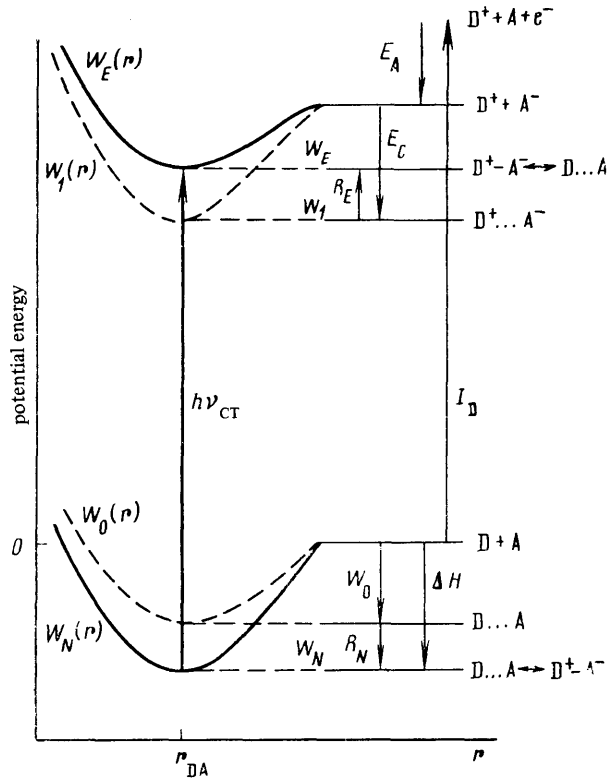


Figure 1. Energy diagram for a weak charge-transfer complex.

Eqn.(5) defines the dependence of the frequency ν_{CD} on the influence of the substituents and the donor, since I_D reflects the change in the donor–acceptor properties of the donor molecule on substitution. This follows, for example, from the Koopmans theorem[12], according to which the ionisation potential of the ith energy level of the molecule is approximately equal to the energy of the corresponding molecular orbital (MO) with the sign reversed.

On the other hand, the Hammett σ constants are traditionally used in physical organic chemistry for the estimation of the effects of substituents. The criterion of the applicability of a particular parameter (including the spectroscopic parameter) to the determination of the dependence of the reactivity of the structure is provided by a linear relation between the parameter and the σ constants[13,14]. It is also necessary that the correlated parameter should have the significance of the Gibbs free energy for the given process. The literature data (see, for examples, Ref.15–17), show the applicability of the Hammett relations to weak donor–acceptor interactions, i.e. the following linear relation holds for the ground states of π,π- and π,σ-complexes (as well as n,σ-complexes [5]):

$$\ln\frac{K_x}{K_0}=\rho_{CT}\sigma \quad , \qquad (6)$$

where K_x and K_0 are the equilibrium constants for the complex formation processes involving substituted (K_x) and (K_0) donors, ρ_{CT} is the reaction constant [corresponding to Eqn.(1)], which depends only on the type of process and characterises the sensitivity of the reaction centre to the influence of substituents, and σ is the constant of the substituent determined by its nature and position in the molecule.

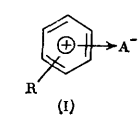
As for the usual chemical processes[13,14], the applicability of Eqn.(6) to the formation of CTC has been studied in detail for benzene derivatives. For three acceptors differing significantly as regards their electron affinities (the affinities[19] E_A are given in brackets), the values of ρ_{CT} (cal mol^{-1}) are as follows[18]: -0.41 for 1,3-dinitrobenzene (0.9), -0.59 for p-chloranil (2.0), and -0.98 for tetracyanoethylene (2,3). The low values of ρ_{CT} indicate a low degree of charge transfer in the ground states of weak CTC and a low sensitivity of the ground states of benzene derivatives (D) to the electronic influence of the substituents in processes of type (1). On transition of the CTC to an excited state, the degree of charge transfer increases sharply (for the excited state of the hexamethylbenzene–tetracyanoethylene complex, it is approximately 0.8 compared with 0.05–0.1 for the ground state[1]).

The values of ρ^*_{CT} (cal mol^{-1}) in the CTS of benzene derivatives (complexes with tetracyanoethylene) are between -10 (Kuznetsov et al.[20]) and -19 (Hanstein et al.[21]). This indicates, firstly, a high sensitivity of the charge-transfer state of the π-donors to the electronic effects of the substituents and, secondly, shows that the use of the excited states of the CTC as a model for the investigation of the mechanisms of certain electrophilic addition reactions is promising because the above values of ρ^*_{CT} are close to the values of ρ for many of the reactions characterised by an ionic transition state. It follows from the principle of the linear free energy relations[13] that[18,21]

$$(h\nu_{CT,x}-h\nu_{CT,0})/(2,3RT)=\rho^*_{CT}\sigma \quad , \qquad (7)$$

where $h\nu_{CT,x}$ and $h\nu_{CT,0}$ (cal) are the energies of the charge-transfer transitions of substituted and unsubstituted donor molecules respectively, R the gas constant, T(K) the absolute temperature, and ρ^*_{CT} (cal mol^{-1}) the reaction constant referring to the formation of an excited CTC. The energy of the charge-transfer transition and the σ constants of the substituents are in this case determined in a liquid solution, i.e. with allowance for the solvation effect.

The structure of the excited state of the CTC involving benzene derivatives is usually represented schematically as follows:



(I)

It is therefore possible to postulate that Eqn.(7) should hold best when the scale of the Brown–Okamoto electrophilic σ^+ constants[22], taking into account the positive charge on the reaction centre (the benzene ring is such a centre in relation to the π-acceptor), is used.

Eqns.(5) and (7) serve as a basis for the quantitative study of the influence of substituents on the reactivity of π-donors in a charge-transfer state. The appearance of a positive charge on the donor centre in the CTS does not significantly diminish the aromatic character of the π-donors. On the other hand, for ethylene derivatives (see below), where the positive charge is localised at the C = C bond, the multiplicity of the latter diminishes sharply in the CTC.[23]

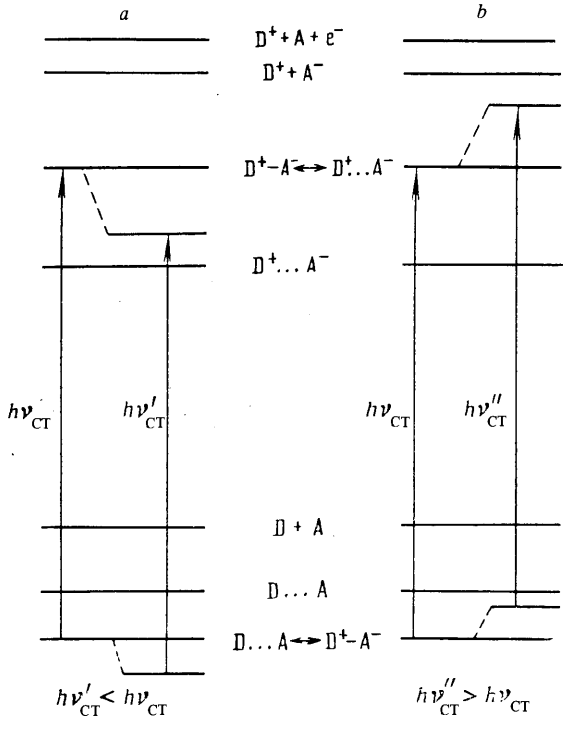
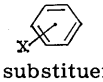


Figure 2. The influence of the electron-donating (*a*) and electron-accepting (*b*) substituents X on the positions of the energy levels in the ground and excited states of CTC for benzene derivatives of the type



a) *+I* or *+M* effect of the substituent; *b*) *–I* or *–M* effect of the substituent.

The influence of substituents on ν_{CT} (in the case of CTC derived from benzene) is illustrated clearly by the energy scheme for the CTC presented in Fig.2. The introduction of an electron-donating substituent increases the electron density in the ring via the inductive (*–I*) on conjugation (*–M*) mechanisms, which stabilises the ground and charge-transfer states of the complex. However, in view of the greater sensitivity of the CTS to electronic effects, already discussed above, the energy of this state diminishes to a greater extent after the introduction of a substituent of this kind. This results in a decrease of the energy of the charge-transfer transition ($h\nu'_{CT}$) of the donor molecule and in a bathochromic shift of the CT band in the electronic spectrum. The introduction of an electron-accepting substituent (with an *–I* or a *–M* effect) has the opposite effect, destabilising the complex and increasing the energies of the ground and charge-transfer states, the latter to a greater extent. This entails an increase of the energy of the charge-transfer transition ($h\nu_{CT}$), which is manifested by hypsochromic shifts of the CT band. The nature of the influence of the electronic nature of the substituent on the energy of the charge-transfer transition follows also from the molecular-orbital study of the formation of the CTC.[24]

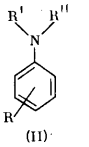
2. Benzene Derivatives

Charge-transfer complexes derived from benzene serve as model compounds for the investigation of many aspects of complex formation[25]. Comparison of the results of the study of the CTC by electronic spectroscopy with data obtained by independent methods makes it possible to obtain information about the mechanisms of the intramolecular interactions in various electronic states.

Such comparative analysis for a series of benzene derivatives has been carried out, for example, by Kuznetsov et al.[26]. The electron density at the donor centre in the CTS has been estimated in terms of the frequency ν_{CT} in the spectra of the complexes with tetracyanoethylene (TCE) and that in the ground state was estimated in terms of $\Delta\nu$, which is the frequency shift of the stretching vibration of the O–H bond of phenol in the infrared spectrum on formation of the O–H...π hydrogen bond between phenol and benzene derivatives. The $\Delta\nu$ and ν_{CT} for a series of compounds are linked by an empirical linear relation

$$\Delta\nu = -0{,}0074\ \nu_{CT} + 237 \qquad (8)$$

which shows that the effects of the substituents in the ground and charge-transfer states do not differ fundamentally. However, the experimental points for compounds with substituents having a lone electron pair (LEP)† [of the type of OCH_3, SCH_3, $N(CH_3)_2$, etc.] or substituents tending to become polarised in the CTS (I, $CH=CH_2$, etc.) deviate from Eqn.(8) towards lower values of ν_{CT}; the deviations δ (kcal mol^{-1}) = $\nu_{CT}^{exp} - \nu_{CT}^{calc}$ are between 10 and 20 kcal mol^{-1}. This is caused by the appearance of the electromeric *+E* effect in the CTS (increase of the n,σ, σ,π, and π,π conjugation as a consequence of the electron density deficit in the benzene ring) and by the significant contribution of the LEP of the heteroatom to the highest occupied molecular orbital (HOMO) in the corresponding compounds. We shall consider in greater detail the intramolecular interactions in the CTS of compounds of the type indicated.



(II)

$R' = R'' = H, CH_3$

†Here and henceforth in this review the $\Delta\nu$ and ν_{CT} are quoted in cm^{-1}.

The frequencies ν_{CT} in the spectra of the CTC of the aromatic amines (II) with TCE are linearly related to the basicity expressed by the pK:[27]

$$pK = -0.449 \cdot 10^{-3}\ \nu_{CT} + 11.05 \quad . \qquad (9)$$

o-Halogenoanilines do not obey this relation. Despite the π,π-character of the complexes of anilines with TCE, in the presence of halogens in the *ortho*-position there is a possibility of a direct overlap of the *p*-orbitals of the halogen atoms and the π-orbitals of the TCE molecule.

Tetracyanoethylene can react with aromatic amines[27] and it is therefore preferable to use weaker π-acceptors, for example, 1,3,5-trinitrobenzene (TNB).[28] The substituents examined by Kravtsov and Faingor[28] included a series of organomercury derivatives, so that information about the donor–acceptor properties of the Hg–X fragment was obtained from the ν_{CT} data. The following relation holds for the CTC of organic derivatives of dimethylaniline and TNB:

$$\nu_{CT} = 2130\sigma_p^+ + 20490;\ \dot{\rho}_{CT} = -4.49^{\dagger} \quad . \qquad (10)$$

It was used to calculate the σ_p^* constants of the substituents[28]. When organomercury substituents are introduced into the ring, the CT band undergoes a hypsochromic shift, which indicates the electron-accepting properties of such substituents. For α-substituted *N*,*N*′-dimethyl-*p*-toluidines, there is a linear relation between ν_{CT} and the inductive σ_I constants of the substituents in the methyl group:

$$\nu_{CT} = 3120\sigma_I + 19550;\ \dot{\rho}_{CT} = -6.58\ (r = 0.971) \quad . \qquad (11)$$

This indicates a predominantly inductive interaction of the substituent with the aromatic ring. An analogous correlation has been obtained for organomercury substituents of the type of HgX with different X:

$$\nu_{CT} = 2880\sigma_I + 19960;\ \dot{\rho}_{CT} = -6.07\ (r = 0.991) \quad . \qquad (12)$$

It follows from Eqns.(11) and (12) that the transmission properties of the mercury atom are weaker than those of the methylene unit.

The spectra of the CTC formed by compounds of the type $C_6H_5ECH_3$ (E = O, S, Se, or Te) (III) have been investigated in fair detail. The electron-donating properties of compounds (III) increase on passing from E = O to E = Te,[29] apparently mainly as a result of the increasing *n*-character of the highest occupied molecular orbital. Indeed the ionisation potentials of the *n* electrons of sulphur, selenium, and tellurium are smaller than the first ionisation potential of benzene and the orbital of the heteroatom therefore makes the main contribution to the HOMO of thio- and seleno-anisoles. The nature of the HOMO of the anisole molecule is determined by the symmetrical π_S-orbital of the ring, because the ionisation potential of the *n* electrons of the oxygen atom is greater than the first ionisation potential of benzene. Nevertheless all compounds of type (III) are donors of the π-type.

The electron-donating properties of the compounds XC_6H_4-ECH_3 (IV) become weaker as the position of X varies in the series *para*- > *ortho*- > *meta*-.[29] Owing to steric interactions, in *ortho*-substituted compounds (IV) there is a possibility of a breakdown of the coplanarity of X and the remainder of the molecule, which leads to an alteration of the electron-donating capacity of the compound as a whole[29,30]. As was to be expected, the electrophilic σ^+ constants proved to be preferable to the usual Hammett σ constants for the description of the correlation with ν_{CT} in the spectra of the CTC formed by compounds (IV).[31,32] The sensitivity of the HOMO to substitution in the ring of compound (IV) diminishes in the series of substituents O > S > Se as a consequence of the increasing localisation of the HOMO at the heteroatom and the appreciable conformational inhomogeneity (see also Vtyurina and Chmutova[34]).

The substituents have a complex influence on the ν_{CT} in the spectra of CTC formed by compounds of the type C_6H_5ER (V).[33] For E = O, the frequencies ν_{CT} vary in the following sequence of R: $CH_3 > C_2H_5 >$ iso-$C_3H_7 \ll$ t-C_4H_9. The sequence R = $CH_3 \cong C_2H_5 <$ iso-$C_3H_7 \ll$ t-C_4H_9 holds for sulphides and selenides. The conformation of the molecules of compounds (V) depends on the nature of E. Planar conformers are obtained for E = O, in which R influences the conjugated system mainly inductively and a non-planar configuration and the steric inhibition caused by this is possible only for R = t-C_4H_9. For E = S or Se, the steric effects of the substituents R are stronger and there is monotonic decrease of the energy of the HOMO with increasing bulk of R.

Variation of the bulk of the group R alters the ratio of the intensities of the long-wavelength and short-wavelength bands in the electron absorption spectra of CTC of compounds (V),[34] as in other benzene derivatives[36,37]. Bulky substituents (of the type of t-C_4H_9) decrease the intensity of the long-wavelength band both as a result of the decrease of the electron-donating capacity of the substituents as a consequence of the decrease of n,π conjugation and as a result of the increase of the contribution of the "transverse" orientation of the complex for steric reasons[35].

In contrast to the isologous anisoles, the intramolecular interactions in the CTS of phenol derivatives have been less thoroughly studied. The following linear correlations between ν_{CT} and σ^+ constants have been established for phenol derivatives:

(a) Monosubstituted phenols[38]:

$$\nu_{CT} = 5000\sigma_p^+ + 20500;\ \rho_{CT}^+ = -10.0\ (r = 0.998)\ ; \qquad (13)$$

(b) *para*-Substituted 2,6-di-t-butylphenols[39]:

$$\nu_{CT} = 2830\sigma_p^+ + 17400;\ \dot{\rho}_{CT}^+ = -5.9\ (r = 0.992) \quad . \qquad (14)$$

A linear relation between ν_{CT} and $\Delta\nu$ (a property of the ground state) holds for monosubstituted phenols[38]. In contrast to benzene derivatives (see above), $\Delta\nu$ represents in this instance the shift of the stretching vibration frequency of the O–H bond in the infrared spectra of phenols on formation of an intermolecular hydrogen bond by the latter with tetrahydrofuran (a characteristic of the acidity of phenols). The points corresponding to compounds containing the O or S heteroatom deviate from the relation

$$\Delta\nu = 0.0194\ \nu_{CT} - 90\ (r = 0.970) \qquad (15)$$

towards lower values of ν_{CT}. The cause of the deviation is the same as for the benzene derivatives examined above—enhancement of the degree of n,π conjugation of the electron-donating substituents on passing from the ground state (+*M* effect) to the CTS (+*E* effect) and the increase of the *n*-character of the HOMO. The presence of even one bulky substituent in the *ortho*-position relative to the OH group alters the nature of the intramolecular interactions in phenol derivatives[40].

The quality of the $\nu_{CT} = f(\sigma^+)$ correlations improve somewhat when σ^+ and σ^- constants are used simultaneously: for more than 30 trisubstituted phenols with two *ortho*-substituents, the following relation holds according to the

---

#Here and henceforth ρ_{CT}^* (cal mol^{-1}) is the slope of the plot of $\nu_{CT} = f(\sigma)$ [see Eqn.(7)].

data of Sennikov et al.[39]:

$$\nu_{CT} = 3840\Sigma(\sigma^+ + \sigma_0) + 18900 \quad . \qquad (16)$$

The considerable role of steric effects in the CTS is also indicated by the absence of a simple relation of type (15) for *ortho*-substituted phenols[40]. The significant decrease of the absolute value of the constant ρ^*_{CT} for shielded phenols [cf. Eqns.(13) and (14)] implies a decrease of the sensitivity of the HOMO of 2,6-di-t-butylphenols to structural changes in the molecule in the CTS, caused evidently mainly by the steric effects of the two t-butyl groups. The absence of fundamental changes in the influence of the *para*-substituent on transition of the molecules of 2,6-di-t-butyl phenols from the ground states to the CTS is indicated by the linear relation between ν_{CT} and the integral intensity $A^{1/2}$ of the ν(O–H) band in the infrared spectra of phenols[39]:

$$A^{1/2}\ (\text{mol}^{-1/2}\ \text{litre}^{1/2}\ \text{cm}^{-1}) = 0.69 \cdot 10^{-4}\nu_{CT} + 0.056\ (r = 0.980). \qquad (17)$$

A property of phenol derivatives which is of practical importance, namely their antioxidant capacity, characterised quantitatively by the rate constant k for the chain termination reaction in the radical oxidations of hydrocarbons [reaction (18)] or some other quantities[43], is linearly related to the energy of the HOMO of phenols[41,42]:

$$R'OO^{\cdot} + ROH \xrightarrow{k} R'OOH + RO^{\cdot} \quad . \qquad (18)$$

This enabled Lloyd[44] and Razuvaev et al.[45] to compare the ν_{CT} in the spectra of the CTC between phenols and TCE with data for the antioxidant activity. There is a parallel variation of ν_{CT} and the residual strain in the polymers, characterising the degree of their degradation[44]. A quantitative relation has also been established[45] between the logarithms of the rate constant of reaction (18) (R′ = styrene) and ν_{CT} in the spectra of the CTC formed by *meta*- and *para*-substituted unshielded phenols and *para*-substituted 2,6-di-t-butylphenols:

$$\ln k \cdot 10^{-3} = -7.67 \cdot 10^{-4}\ \nu_{CT} + 16.70\ (r = 0.999)\ ; \qquad (19)$$

$$\ln k \cdot 10^{-3} = -10.13 \cdot 10^{-4}\ \nu_{CT} + 18.80\ (r = 0.996)\ . \qquad (20)$$

These results make it possible to regard ν_{CT} as a characteristic of the inhibiting capacity of phenolic antioxidants.

The study of the intermolecular interactions in the CTS of the ether XC_6H_4-OR (R is a constant fragment capable of conjugation with the heteroatom), can yield information about the involvement of the heteroatom (oxygen) in the transmission of conjugation effects. The nature of the conjugation effects in molecules of *para*-substituted phenyl vinyl and isobutenyl phenyl ethers XC_6H_4-O-CH = $C(CH_3)_2$ (VI) has been considered by quantum-mechanical methods, by the spectroscopy of the CTC with TCE, and by kinetic procedures[46,47]. A linear relation between the energy of the HOMO and the σ_p^+ constants of the constituents in the benzene ring follows from the calculations of the electronic structure in the ground state of phenyl vinyl ethers[47]:

$$E_{HOMO} = 0.58\sigma_p^+ + 10.92. \qquad (21)$$

This molecular orbital is localised mainly on the oxygen atom and on the alkene carbon atoms. There is a linear correlation between $h\nu_{CT}$ and the σ_p^+ constants for compounds (VI)¶:

$$h\nu_{CT} = 0.56\sigma_p^+ + 2.39;\ \rho^{\cdot}_{CT} = -9.4\ (r = 0.990)\ . \qquad (22)$$

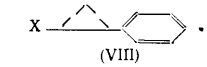
According to Donnay et al.[46], the similar slopes of relations (21) and (22) confirm the presence of a common conjugational system in molecules of isobutenyl phenyl ether (VI) [we may note that the correlation expressed by Eqn.(22) apparently refers to the CTS and not to the ground state of the molecule of compound (VI) as suggested by Donnay et al.[46]]. Quantum-mechanical calculations on analogous molecules[29] also indicate the presence of a single conjugated aromatic ring–heteroatom–double bond system in which the nature of the HOMO is determined by the interaction of the heteroatom not only with the ring but also with the α,β-double bond (in contrast to, for example, allyl derivatives where the influence of the double bond in the β,γ-position relative to the heteroatom is of subsidiary importance). However, the contribution of the heteroatom to the HOMO (i.e. its involvement in the transmission of conjugation effects) becomes significant only for C = S or Se. As already mentioned, for ethers the contribution of symmetrical π_S-orbitals of the ring predominates. This was confirmed by the impairment of the correlation between ν_{CT} and the σ^+ constants on passing from ethers to selenides. The role of the conformational effect increases in the same sequence[31]. The high accuracy of correlation (22) therefore indicates that the coordination of the TCE molecule to the benzene ring predominates.

The intramolecular interactions in the CTS of aryl benzyl ethers $C_6H_5CH_2OC_6H_4X$ (VII) have been investigated[48]. In this case the correlation between $h\nu_{CT}$ and σ^+ is

$$h\nu_{CT} = 0.45\sigma_p^a + 2.40;\ \rho^+_{CT} = -7.66\ (r = 0.970)\ . \qquad (23)$$

Unfortunately we are unaware of studies devoted to complexes of derivatives of diphenyl ether with TCE. Comparison of such data with the above results[48] would enable one to elucidate the role of the methylene unit in the transmission of electronic effects in the CTS.

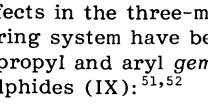
Brown and Treylor[49] examined the intramolecular interactions in the CTS of 2-substituted phenylcyclopropanes (VIII):



(VIII)

It follows from the electronic spectroscopic data for the CTC of these compounds with TCE that the cyclopropyl group is a much more powerful electron donor than, for example, the ethyl group. The authors[49] attribute this to the σ,π conjugation of the cyclopropane and benzene fragments. However, the substituents X in the 2-position in the three-membered ring (for example, the methoxy-group) hardly influence the donor–acceptor properties of the molecule of compound (VIII) in the CTS. From this, one can conclude that the ability of the cyclopropyl group to transmit the π-electronic effect in the CTS is negligible, which is confirmed by the results of Mancini et al.[50]

The conjugation effects in the three-membered ring–heteroatom–benzene ring system have been considered in relation to aryl cyclopropyl and aryl *gem*-dichlorocyclopropyl ethers and sulphides (IX):[51,52]



(IX)

$R^I = R^{II} = H, Cl;\ E = O, S$.

The ν_{CT} data for the complexes of compound (IX) with TCE (classified as of the π,π-type) indicate the electron-accepting properties of the cyclopropane fragment of the molecule of

¶Here and henceforth the values of $h\nu_{CT}$ are expressed in eV.

compound (IX) in the CTS, which is determined by both the inductive ($-I$) and conjugation effects.

The intramolecular interactions in phenyl derivatives of group (VIa) elements of different complexity have been investigated in a series of studies[53-56,59] (data for the ν_{CT} and the equilibrium constants K_C for complexes with π- and σ-acceptors were used). It was shown that the electron-donating properties of the diaryl ethers, sulphides, and selenides as well as the stability of their complexes with iodine (CTC of the n,σ-type) become enhanced in the sequence O (K_C = 0.39 litre mol^{-1}; ν_{CT} = 29000 cm^{-1}) < S (3.90; 28600) < Se (27.8; 28200).[54] The increased stability of the selenium complexes compared with the sulphur-containing analogues is due to the high basicity and large size of the selenium atom[53,54]. The equilibrium constants for the CTC of substituted diphenyl sulphides increase with decrease of ν_{CT}, i.e. as the electron-donating properties of the sulphides become more pronounced[54]. The quantity ρ_{CT} for the correlation between $\lg K_C$ and σ for diphenyl sulphides (−0.54) is somewhat smaller than the corresponding values for thiophenols (−1.11).[53] This is associated with the smaller change in electron density at the sulphur atom under the influence of substituents as a consequence of the conjugation intramolecular transmission of the electronic effects between the two phenyl groups via the bridging sulphur atom. Another cause of the decreased sensitivity of diphenyl sulphides to structural changes is apparently associated with the steric hindrance by the phenyl groups of the approach of the σ-acceptor to the reaction centre (the sulphur atom).

The ability of the selenium bridge to transmit the electronic effects between two aromatic systems is much smaller than that of the sulphur-containing bridge, which can be seen from the high value $\rho = -2.1$ for diphenyl selenides, indicating a high sensitivity of the electron density at the selenium atom to external perturbations. The introduction of a methylene fragment between the heteroatom and the benzene ring (the CTC of aryl benzyl sulphides with iodine[54,57]) disturbs the transmission of electronic effects described above. The study of the spectra of the CTC of diphenyl sulphides with TCE showed[55,56] that *para*-substituted sulphides exhibit the most marked electron-donating properties as a consequence of the direct polar conjugation of the LEP of the heteroatom with *para*-substituents (Cl, OCH_3, etc.) via the π-electron system, mentioned above for thio- and seleno-anisoles. The anomalously weak electron-donating properties of bis(*o*-dimethylphenyl) sulphide (compared with those of alkyl sulphides) have been considered[55] as a result of the breakdown of the conjugation of the LEP of the sulphur atom with the two benzene rings. The marked conformational changes in such compounds have been confirmed by data obtained by independent methods[58]. The correlation between $\lg K_C$ and the σ constants of TCE is characterised by $\rho = -0.74$, which is close to $\rho = -0.64$ obtained for the CTC of the same sulphides with iodine[54]. This result suggests that the HOMO in these and other complexes are isotypical.

It is known[1] that the K_C for the complexes of typical π-donors with TCE are higher than for CTC with I_2. As the n-donor character is enhanced, the K_C of the complexes with iodine increase and for the pure n-donors they are much higher than the K_C for the complexes with TCE. The K_C for the complexes of diphenyl sulphides[55] with iodine are somewhat higher than those for the complexes with TCE, which indicates a mixed n,π-character of the HOMO of diphenyl sulphides.

This problem has been considered in more detail in relation to aryl diphenylmethyl sulphides $X^1C_6H_4(X^2C_6H_4)CHSC_6H_4Y$ (X).[56,59] The two phenyl fragments and the thiophenyl system are in this instance potential donor centres. Analysis of the ν_{CT} and the K_C for the complexes of compounds (X) with TCE and iodine shows that electrophilic attack by the iodine atom is directed preferentially to the sulphur atom (HOMO of the n,π-type) and not to the diphenylmethyl system. The effect of the substituent X is determined by the inductive mechanism and the sensitivity of the complex formation reaction with I_2 to the influence of the substituent is low because of the long distance between the substituent and the sulphur atom. The fragment Y acts on the sulphur atom via both inductive and resonance mechanisms and the resulting effect is approximately four times greater. The interaction of compounds (X) with a π-acceptor (TCE) is of an appreciably more complex type: TCE interacts with both the phenylthio-system and with the diphenylmethyl group.

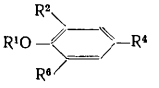
The intramolecular interactions in large series of disulphides and diselenides of the type $X-C_6H_4-E-E-C_6H_4-X$ (XI, E = S or Se) have been investigated[60]. Whereas the CTC of aromatic disulphides with I_2 have not been detected spectrophotometrically[53], the complexes of diaryl diselenides absorb in the range 270–390 nm. The linear relation between ν_{CT} and σ^+ is characterised by the quantity ρ^*_{CT} = −2.0. According to the authors[60], in the case of compounds (XI) a single molecular orbital, incorporating not only the central fragment $-C_6H_4-Se-Se-C_6H_4-$ of the test molecules but also the substituents X, is involved in the formation of complexes. As in the monosulphides and monoselenides, in aromatic disulphides and diselenides the intramolecular interactions are strongly manifested between substituents in the *para*-positions in the benzene rings. The sharp difference between the electron-donating properties of diaryl disulphides and diaryl diselenides in relation to iodine can be explained by the fact that the LEP of the sulphur atoms in the $(XC_6H_4)_2S_2$ molecules are incorporated to a greater extent in the π-system of the conjugated multiple bonds compared with the $(XC_6H_4)_2Se_2$ molecules. Comparison of the reaction constants for the CTC of compounds (XI) with TCE (ρ^*_{CT} = −2.89 for the sulphides and −2.04 for the selenides) indicates a somewhat greater sensitivity of the sulphur-containing compounds to the electronic effects of substituents (an analogous relation has been observed also for thio- and seleno-anisoles). The sensitivity of the disulphides greatly increases (ρ^*_{CT} = −7.32) when one of the phenyl groups in compounds (XI) is replaced by a methyl group.

We shall now consider the intramolecular interactions in the CTC of aryl derivatives of Groups IVB elements. In view of the lower electronegativity of the silicon atom (1.9) compared with that of carbon (2.6) [61] and the high inductive constant of the trimethylsilyl group [$\sigma^* = -0.9$ compared with $\sigma^* = -0.3$ for $C(CH_3)_3$],[63] an enhancement of the electron-donating properties of organosilicon derivatives compared with their carbon analogues may be expected. However, the results of spectrophotometric studies on the CTC of the compounds C_6H_5-X (XII) indicate the opposite situation[62]. This finding can be accounted for by the manifestation of the effect of the $d_\pi-p_\pi$ interaction due to the partial transfer of the π-electron density from the benzene ring to the vacant 3*d* orbitals of silicon, which acts in opposition to the $+I$ effects of the silyl groups.

Different aspects of this effect have already been considered[64]. The group $CH_2Si(CH_3)_3$ has more marked electron-donating properties than the trimethylsilyl group. Thus the following series based on the variation of the electron-donating properties of compounds (XII) as a function of X has been established: $CH_2Si(CH)_3 > CH_3 >$

$Si(CH_3)_3$; it is valid also for compounds containing several substituents in the ring[62].

Different aspects of the effects of the d_π–p_π interaction and σ,π conjugation in the charge transfer state have been considered[65–67].



(XIII)

Analysis of the values of ν_{CT} in the sterically hindered organosilicon phenols and ethers (XIII) shows[68] that the replacement of the $(CH_3)_3C$ group by $Si(CH_3)_3$ leads to an increase of ν_{CT} and hence to an enhancement of the electron-accepting properties of the phenols (in relation to the larger series of organosilicon and organogermanium phenols, this problem has been considered by Sennikov et al.[39]). An analogous relation has been observed also for the organosilicon ethers [$R^1 = Si(CH_3)_3$]; comparison of the values of ν_{CT} for the latter with the ν_{CT} for phenols shows that the trimethylsilyl group of the $Ar–O–Si(CH_3)_3$ fragment is a stronger electron acceptor than $C(CH_3)_3$ or the hydrogen atom.

Consequently the effect of the d_π–p_π interaction does not remain unchanged and depends significantly on the nature of the substituent X in the $(CH_3)_3Si$-X fragment. This observation has been confirmed by the study of the CTC of *para*-substituted organosilicon ethers p-XC_6H_4–O–Y (XIV) (compared with anisoles).[69,70] Whereas compounds (XIV) with $Y = Si(CH_3)_3$ exhibit weaker electron-donating properties compared with anisoles, with $Y = CH_2Si(C_2H_5)_3$ there is a considerable enhancement of the π-donor properties. The separation of the oxygen and silicon atoms by the $-CH_2-$ group disturbs the d_π–p_π interaction of the LEP of the oxygen atom with the 3*d* orbitals of silicon[71], which is manifested by a lower sensitivity of the HOMO of the molecule of compound (XIV) with $Y = CH_2Si(C_2H_5)_3$ to the electronic effects of substituents compared with compounds (XIV) in which $Y = Si(CH_3)_3$.

Analysis of the donor–acceptor properties of organosilicon ethers with the groups O–Si≤, O–Si–Si≤, and O–CH_2–Si≤[71] leads to the conclusion that the *n*-orbital of the oxygen atom interacts with the π_s-orbital of the benzene ring. The influence of the organic substituent R in C_6H_5OR on the nature of the HOMO is weak and is transmitted mainly via the inductive mechanism. It is believed essential[71] to take into account the interaction of the LEP of the oxygen atom with the σ orbitals of the neighbouring C–Si or Si–Si bonds in the ethers with $R = Si(CH_3)_3$, $CH_2Si(CH_3)_3$, or $Si_2(CH_3)_5$ (taking into account photoelectron spectroscopic data).

The electronic absorption spectra of the CTC of more than 70 organosilicon and organogermanium derivatives of benzene with TCE have been considered in a number of studies[65–67], where the electronic effects of the organoelemental substituents in the ground and charge-transfer states were also compared. The donor–acceptor properties of the compounds in the ground states were characterised in terms of the quantity $\Delta\nu$ (see above). The points corresponding to compounds with substituents whose degree of conjugation with the ring does not change significantly on transition from the ground to the charge transfer state fit on the plot of Eqn.(8) described above. Such substituents include also fragments with the M–Ar bond (M = Si or Ge), which indicates the constancy of the manifestation of the d_π–p_π interaction in the ground and charge transfer states. The points corresponding to the benzyl derivatives of silicon and germanium deviate from correlation (8) towards lower values of ν_{CT} (analogously to the derivatives of benzene with substituents containing a heteroatom with LEP). The anomalously pronounced electron-donating properties of benzyl derivatives can be explained by the effect of the σ,π conjugation of the C–M bond with the benzene ring in the CTS.[65] For the benzyl derivatives of silicon and germanium, the σ,π conjugation occurs even in the ground state but, on passing to the CTS, it becomes much more marked[67]. The effect of the σ,π conjugation is impaired after the introduction of a second methylene group into the molecule (compounds of the type $C_6H_5CH_2CH_2MR_3$).[72] The degree of σ,π conjugation diminishes following the enhancement of the electron-accepting properties of the substituents at the atom M.[73]

Specific electronic effects obtain for organosilicon derivatives of benzene with an Si–Si bond. Recently the interaction of the Si–Si σ-bond with unsaturated fragments has been studied by various physical methods, including spectrophotometry of the CTC.[62,74–78] Analysis of the CT band in the electronic spectra of complexes of benzene derivatives containing the SiR_2SiR_3 and CH_2SiR_3 groups has shown[62] that the ν_{CT} of the long-wavelength bands corresponding to these compounds are 20200 and 20400 cm^{-1} respectively. Thus the disilanyl substituent exhibits the same σ-donor properties as the trimethylsilylmethyl substituent, the properties being more marked than the electron-accepting properties of the same fragment due to the d_π–p_π interaction. Subsequent studies[74–78] confirmed the occurrence of σ(Si–Si)–π conjugation in phenylpolysilanes. The electron-accepting properties of fragments containing the polysilicon chain are apparently determined by the silicon atom which is closest to the benzene ring[78].

The determination of the coordination centre of the π-acceptor (TCE) in the study of the intramolecular interactions in the π-complexes of metals (data for the CTC of cyclopentadienyl derivatives of iron, cobalt, and nickel[4,79]) has been the subject of controversy; the problem was whether this centre is the cyclopentadienyl ring or the metal atom[80,81]. The authors of two reviews[4,79] believe that the compounds most probably form complexes of the π,π-type. This question has been investigated for arenechromium, arenemolybdenum, and arenetungsten tricarbonyls of the type $XC_6H_5M(CO)_3$ (XV, M = Cr, Mo, or W).[82–86] It has been concluded[83,84] that there are two coordination centres in arenemetal tricarbonyls—the benzene ring in complexes with TNB and the metal atom in complexes with TCE. However in other studies[85,86] data for the CTC spectra have been interpreted from the standpoint of the coordination of both π-acceptors solely to the aromatic ring.

The following relations have been obtained for the complex-formation reactions of arenechromium tricarbonyls with TNB (a weak π-acceptor) and TCE (a strong π-acceptor):[86]

$$\text{TNB}: \nu_{CT} = 1060\Sigma\sigma^+ + 20700;\ \rho^*_{CT} = -2.23\ (r = 0.870)\ ; \quad (24)$$

$$\text{TCE}: \nu_{CT} = -1550\,\Sigma\sigma^+ + 13300;\ \rho^*_{CT} = +3.27\ (r = 0.950). \quad (25)$$

The inversion of the sign of the reaction constant ρ^*_{CT} on passing from complexes with TNB to those with TCE indicates a change in the mechanism of the transmission of electronic effects. This change is associated with the ability of the $Cr(CO)_3$ group to manifest electron-accepting properties in the presence of a fairly small positive charge on the ring (complexes with TNB, $\rho^*_{CT} < 0$) and electron-donating properties when there is an appreciable deficit of electron density at the donor centre (complexes with TCE, $\rho^*_{CT} > 0$). For CTC with *p*-chloranil, *p*-bromanil. and trinitrophenol, which have intermediate E_A values, the correlation between ν_{CT} and σ^* constants is impaired, which indicates a smooth

variation of the mechanism of the transmission of the electronic effects in the system $Cr(CO)_3$ group–benzene ring–π-acceptor. The following series based on the enhancement of the electron-accepting properties of arenemetal tricarbonyls has been obtained from spectrophotometric data for the CTC of compounds (XV) with TCE:[86] Cr < Mo << W.

Relations of the type $\nu_{CT} = f(\sigma)$ make it possible to apply the spectrophotometry of the CTC to the evaluation of the σ constants of the substituents. It was shown in the introduction to this review that the greatest efficiency of this method is to be expected in the calculation of the σ^+ constants. On the other hand, the possibility of using this method also for the determination of σ constants using the equation

$$\nu_{CT} = 10\,000\,\Sigma\sigma + 23\,900 \quad . \qquad (26)$$

has likewise been demonstrated[87,88].

Eqn.(26) holds only for benzene derivatives without substituents whose electronic influence increases sharply on transition from the ground to the charge-transfer state. Otherwise one must employ either the equation[21]

$$\nu_{CT} = 9200\sigma_p^+ + 26200 \quad , \qquad (27)$$

or, according to Kuznetsov et al.[65], the equation

$$\nu_{CT} = 5260\sigma_p^+ + 24800 \quad . \qquad (28)$$

The significant difference between the slopes of relations (27) and (28) can be explained by the different methods used to derive them. Eqn.(27) has been derived for several benzene derivatives containing substituents with known σ^+ constants in the range 0 to −1.4, while Eqn.(28) has been obtained by combining two equations[87,88]:

$$I_D\ (eV) = 0.80\sigma_p^+ + 9.67 \quad ; \qquad (29)$$

$$\nu_{CT} = 7500\ I_D - 41\,000, \quad . \qquad (30)$$

Eqn.(29) is valid only for mono- and di-substituted benzenes. When the equation for a large series of polysubstituted benzenes[89] is used instead of Eqn.(29), the numerical values of the parameters in Eqn.(28) approach those in Eqn.(27). Despite these deficiencies, Eqns.(27) and (28) are used to calculate the σ_p^+ constants for different substituents, including organoelemental substituents[21,65,90].

An attempt has been made to calculate the inductive σ_I constants of substituents of the type CH_2CR_3 from spectrophotometric data for CTC.[91]

3. Naphthalene Derivatives

There are a number of reviews on the CTC of naphthalene derivatives[1,2,4], but the available data on the intramolecular interactions in the CTC of these compounds are fragmentary. In contrast to the benzene derivatives[92,93], the electronic absorption spectra of the CTC of substituted naphthalenes exhibit three bands (which is consistent with the molecular orbital theory[62]), the third shortest-wavelength band having a very low intensity. The influence of the substituents on the first and second CTC bands is analogous to that of benzene but the sensitivity to this influence of the charge-transfer transitions corresponding to these bands depends on the type of substitution (see, for example, Evans et al.[94]). The introduction of both the $C(CH_3)_3$ and $Si(CH_3)_3$ groups increases the energy of the HOMO of naphthalenes (compared with the unsubstituted derivatives) as a consequence of the inductive +*I* effect (the bathochromic shift of both bands in the spectrum corresponds to this)[94]. However, despite the large +*I* effect of the trimethylsilyl group for organosilicon derivatives, a large bathochromic shift of the CT bands is not observed owing to the effect of d_π–p_π interaction in silylnaphthalenes.

Analysis of the ν_{CT} data also shows that, for 1-, 1,4-, and 1,5-substituted derivatives, the first (long-wavelength) band is more sensitive to the electronic influence, whereas for 2-, 2,6-, and 2,7-derivatives the second (short-wavelength band) is more sensitive. The effect of the d_π–p_π interaction in naphthalene derivatives has also been studied by Kuznetsov et al.[95]; it was found that 1-substituted derivatives have more pronounced electron-donating properties than 2-substituted derivatives, which agrees with the data of Evans et al.[94] The NH_2, OCH_3, and OH groups are significantly stronger electron donors in relation to the hydrogen atom than the $Si(CH_3)_3$ group, which again indicates the d_π–p_π interaction between the 3*d* orbitals of the silicon atom and the naphthalene ring.

The study of the intramolecular interactions in the CTC of 1-substituted naphthylpolysilanes[78] established the following series based on the enhancement of the electron-donating properties of the substituents: H < $Si(CH_3)_3$ < CH_3 < $Si_2(CH_3)_5$ < n-$Si_3(CH_3)_7$ < iso-$Si_3(CH_3)_7$ < $Si(CH_3)_3CH_2$. In contrast to benzene polysilicon compounds, the ionisation potential of the naphthalene system (8.12 eV) is lower than that of the σ-system of the substituents, including polysilanes: 8.69 eV for $Si_2(CH_3)_6$ and 8.19 eV for $Si(CH_3)_3$.[78] Therefore, when the molecular σ- and π-orbitals in naphthylpolysilanes overlap, the HOMO is mainly of the π-character. The data for the CTC spectra of 1- and 2-substituted naphthylpolysilanes have been discussed[96] from the standpoint of the σ,π conjugation of the Si–Si bond with the π-system of the naphthalene ring, but the authors unjustifiably neglected the d_π–p_π interaction.

4. Derivatives of Ethylene and Cyclopropane and Saturated Compounds

The study of the spectra of the CTC of alkyl vinyl ethers CH_2 = CH–OR (XVI) with TCE established[97] that the electron-donating properties of compounds (XVI) in the CTC increase in the following sequence of R: CH_3 < C_2H_5 < iso-C_3H_7 < t-C_4H_9, which agrees with the reactivity data[97]. We may note that a somewhat different relation has been observed for compounds (V), which are formal analogues of compounds (XVI). The view[97] that in alkyl vinyl ethers (in contrast to the aromatic analogues) the effects of the conjugation of the alkoxy-group with the double bond play a secondary role must be regarded as insufficiently well founded from the standpoint of the results of the study of Lopatin et al.[98].

Comparison of the frequencies ν_{CT} in the spectra of the CTC of the alkenyl derivatives of silicon of the type CH_2 = CH–$(CH_2)_n$–SiR_3 (XVII) (*n* = 1, 2) and the related carbon compounds with TCE on the basis of the results of Kuznetsov et al.[99] does not rule out the possibility of an interaction of the d_π–p_π type between the Si–C and C = C bonds for *n* = 1 in the CTS. In reality the usual σ,π conjugation is evidently an interaction of this type. A comparative study of the intramolecular effects in the alkenyl derivatives of carbon, silicon, germanium, and tin in the ground and charge-transfer states has been carried out[98]. The electronic influence of the substituents in the ground state was characterised, as for benzenes[26], by the frequency shift Δν of the stretching vibration of the O–H bond in the infrared spectrum of phenol (an electron acceptor) when it forms hydrogen bonds with the π-systems of ethylene derivatives. The electronic effects in the CTS are characterised by the value of ν_{CT} in the spectra of the CTC with iodine.

The data of Lopatin et al.[98] indicated an important role of the effects of the d_π–p_π interaction and σ,π conjugation in the ground and charge-transfer states. The electronic effects in the ground and charge-transfer states of a number of compounds are linearly related:

$$\Delta\nu = -0.00806\ \nu_{CT} + 342\ (r = 0.980). \qquad (31)$$

In contrast to the benzyl derivatives of silicon and germanium, the experimental points for the alkyl derivatives are consistent with Eqn.(31), which indicates the absence of a sharp increase of the effect of the σ,π conjugation in the allyl derivatives of the elements of the silicon subgroup on transition from the ground to the charge-transfer state. A number of features, which have not been noted for benzene derivatives, have been observed for ethylene derivatives[26], which is associated[98] with the lower multiplicity of the carbon–carbon bond compared with the π-system of the benzene ring in the CTS. The substituent $(CH_3)_3SiSi.(CH_3)_2$ participates in two opposite effects of conjugation with the multiple bond: the d_π–p_π effect (electron accepting) and the σ,π effect (electron donating)[98]. According to some data[77,78], the influence of the second effect predominates.

Cyclopropane and its organic and organosilicon derivatives also form CTC with iodine[1,99]. As the electron-accepting properties of the substituent at the silicon atom linked to the cyclopropane ring are enhanced, a hypsochromic shift of the CT band is observed. The introduction of the methyl group into the cyclopropane fragment is accompanied by a decrease of ν_{CT} and in the presence of electron-accepting fluorine atoms in the three-membered ring ν_{CT} increases. Consequently, despite the specific electronic structure of cyclopropane and its derivatives[100], the nature of the influence of the substituents in the cyclopropane fragment (not containing the benzene ring—this case was examined above) on the position of the band in the spectra of the CTC of these compounds is the same as for the typical π-donors (benzene, naphthalene and ethylene derivatives).

Similar relations have been established also for the interaction of π- and σ-acceptors with saturated compounds of Group IVB metals: permethylpolysilanes[74–78], polygermanes[101], hexamethyldistannanes[101–103], and tetra-alkyl derivatives of germanium, tin, and lead[101,104,105]. Saturated tetra-alkyl monosilanes do not form complexes with TCE apparently as a consequence of the fairly high ionisation potential of the Si–C bond. However, it has been shown[106] that the marked distortion of the valence angles of the atoms involved in the formation of small rings with participation of silicon atoms leads to an appreciable decrease of the ionisation potentials of the corresponding monosilanes (the ionisation potential of 1,1-dimethyl-1-silacyclobutane is 9.4 eV compared with 10.5 eV for tetramethylsilanes[107]).

The silacyclobutanes  –SiRR′ formed give rise to CTC with TCE and there is a linear relation between ν_{CT} and the sum of the inductive constants of the substituents R and R′ at the silicon atom

$$h\nu_{CT} = 2.38\ \Sigma\sigma_{IR,R'} + 3.56\ . \qquad (32)$$

Information about the d_π–p_π interactions has been obtained in the study of complexes of saturated silicon-containing sulphides R–S–R′ (XVIII) with TCE.[108] The attachment of silicon to the sulphur atom lowers the energy of the orbital occupied by the LEP of sulphur, which is manifested by hypsochromic shifts of the CT band and indicates the operation of the effect of the d_π–p_π interaction. This interaction breaks down when the silicon and sulphur atoms are separated by the $-CH_2$-fragment.

Electronic absorption spectroscopy of CTC has also been used to study the electronic structure of the silatranes

$RSi(OCH_2CH_2)_3N$ (XIX).[109–112]

5. Heterocyclic Compounds

In contrast to benzene derivatives, the electronic effects in the CTS of heteroaromatic compounds with an excess of π-electrons[113] have been less thoroughly investigated (see the review on the CTC of pyrrole derivatives[114]). A comparative study of the CTC of five-membered heterocycles with various π-acceptors[115,116] established that the π-donor capacity falls in the sequence pyrrole > furan ≥ thiophen and all the heterocycles are stronger electron donors than benzene. On the other hand, the stability of the CTC of benzene with TCE (the K_C constant) is higher, probably as a consequence of more favourable conditions for the mutual overlap of the orbitals.

Analysis of the values of ν_{CT} and K_C for thiophen, selenophen, and tellurophen[117,118] as well as photoelectron spectroscopic data (ionisation potentials) indicate unambiguously the π-character of the HOMO of thiophens. The π,σ-character of the CTC of thiophens with iodine is demonstrated by the different nature of the variation of the K_C for methyl-substituted thiophens and pyrroles. The K_C for the latter decrease in the sequence of substituents $3\text{-}CH_3 > 2\text{-}CH_3 > H > 2,6\text{-di-}CH_3$, which agrees with the increase of the steric hindrance around the reaction centre (the nitrogen atom). On the other hand, the K_C for the series of thiophens increase in the same sequence, which corresponds to the predominance of the electronic effects over steric effects. This is also indicated by the appreciably different equilibrium constants for the complex-formation reactions of thiophen ($K_C = 0.61$ mol^{-1}), pyridine ($K_C = 160$ mol^{-1}), and tetrahydrofuran ($K_C = 315$ mol^{-1}) with I_2.

It has been established that[118] the following relation holds for the CTC of thiophens and benzenes with TCE:

$$\lg K_C^t = 0.9 \lg K_C^b + 0.2\ . \qquad (33)$$

The slope, which is close to unity, indicates the similarity of the HOMO of the two classes of the compounds. A linear relation has also been established between $\lg K_C^t$ and the Hammett σ constants[118] ($\rho_{CT} = 1.6$). In the CTC with TCE, iodine, and chloranil the HOMO is of the mixed n,π-type.[11] On passing to 5,5-dimethyl-2,2-bithienyl the CTC are stabilised by the $+I$ effect of the methyl group. It follows from the K_C for bithienyl and methylthiophen that the conjugation of the two thiophen rings in 2,2-bithienyl increases the basicity of the donor to a greater extent than the $+I$ effect of two methyl groups.

It has been remarked that[120] examination of the intramolecular interactions of thiophen derivatives in CTC is important for the understanding of the mechanism of the adsorption of these compounds on silochrome in experiments on gas-adsorption chromatography. Furan and thiophen derivatives in CTC exhibit approximately the same electron-donating properties[115,116,118]. The fact that 2-phenylfuran is a stronger electron donor than furan confirms, according to Eittah and Hamed[121], the formation of CTC of the π,π-type. The low frequencies ν_{CT} indicate significant conjugation effects in 2-phenylfuran, which confirms indirectly the planar structure of this molecule. The conjugation effects

are enhanced on passing to 2,5-diphenylfuran, whose molecule is evidently also planar. The conclusion that phenylfurans have a quasi-rigid structure, reached on the basis of electronic spectrosopic data for CTC,[121] has been confirmed by quantum-mechanical calculations.

The intramolecular interactions in the CTC of organic and organoelemental derivatives of thiophen and furan have been investigated systematically[122–124]. The replacement of the methyl group in methylthiophen by the $Si(CH_3)_3$ group leads to an appreciable weakening of the electron-donating properties of the compound. Thus the effect of the d_π–p_π interaction, opposed to the *+I* effect of the silyl groups, is characteristic of derivatives of thiophen as well as the derivatives of benzene, naphthalene, and ethylene discussed above. The electronic effects of the substituent in the CTS of thiophen derivatives have been compared with the electronic effects in the ground state (investigated by measuring the chemical shift τ using NMR data).[123] For a series of compounds, the values of τ and ν_{CT} are linearly related:

$$\tau\,(\text{p.p.m.}) = 6.30 - 0.00015\,\nu_{CT} \quad . \qquad (34)$$

The linear relation shows that the electronic effects of the substituents do not change fundamentally on passing from the ground to the charge-transfer state. The points corresponding to compounds with thienyl substituents deviate from relation (34) towards lower values of ν_{CT}, indicating an increase of the effect of the n,π conjugation of the substituents with the ring in the CTS (the *+E* effect).

The observed relations are similar to those discussed above for benzene derivatives[26]. At the same time, in contrast to benzene derivatives, an increase of the degree of the d_π–p_π interaction between the 3*d* orbitals of the silicon atoms and the π electrons of the thiophen ring has been observed in the CTS of substituted thiophen. This effect is manifested only in the presence of two electron-accepting substituents in the thiophen ring. The values of ν_{CT} in the spectra of the CTC of organoelemental derivatives of thiophen and furan with TCE [122–124] indicate a diminution of the electron-accepting properties of the elements of the silicon subgroup in the sequence Si > Ge > Sn, which is analogous to that for derivatives of benzene and determined by the effect of the d_π–p_π interaction, which weakens on passing from silicon to tin.

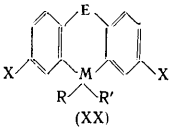
An analogy with benzene derivatives is also observed as regards the sharp enhancement of the electron-donating properties in the CTS of derivatives with substituents of the type $CH_2Si(CH_3)_3$, which is a consequence of the σ,π conjugation. The frequencies ν_{CT} of thiophen and furan derivatives are linearly related[124]:

$$\nu_{CT}^{t} = 0.46\nu_{CT}^{f} + 11000 \quad . \qquad (35)$$

The relation describes compounds with both organic and organoelemental substituents. Despite the lower ionisation potential of thiophen compared with furan[125], thiophen derivatives with electron-donating substituents [CH_3–, $C(CH_3)_3$–] have greater and not smaller frequencies ν_{CT} compared with their furan analogues. The reason for the inversion of the ν_{CT} in thiophen and furan derivatives is the greater sensitivity of the HOMO of furan derivatives to the influence of ring substituents[124]. According to some data[125,126], the sensitivity of the HOMO of aromatic compounds to the influence of substituents varies in the sequence furan > pyrrole > thiophen > benzene.

Derivatives of tetrathiafulvalene and tetrathiatetracene as well as certain other sulphur-containing heterocycles have attracted attention recently in connection with the discovery of conducting properties in their crystalline CTC and radical-ion salts[127,131]. These investigations established in particular[128] that the radical-ion salts derived from compounds in which there is a maximum charge transfer from the donor to the acceptor (tetracyanoquinodimethane) in liquid solution have high conductivities. Consequently the properties of molecular complexes in the liquid solution predetermine the conducting properties of the compounds formed from the given series of components in the solid phase.

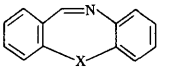
The spectra of the CTC of heterocyclic anthracene-like compounds of type (XX) have been investigated in a series of studies[132–134]:



(XX)

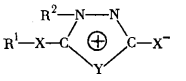
E = N – C_2H_5, O, S;
M = Si, Ge, Sn;
R, R' = CH_3, C_6H_5, H .

The joint analysis of ν_{CT} data[133,134], the ionisation potentials[135], and the results of X-ray diffraction analysis[136,137] of these compounds has shown that the enhancement of the electron-donating properties takes place in parallel with the increase of the dihedral angle between the rings. The latter corresponds to an approach of the molecular skeleton to the planar structure and to an increase in the degree of conjugation in the sequences O < S < N and Sn < Ge < Si. As already mentioned, similar relations hold for phenylfurans[121]:



(XXI)

X = CH_2, O, S, NCH_3, C=O



(XXII)

X = O, S, $NCOR^1$, $NCSR^2$,
Y = O, S, NR^2, NH_2 .

The linear correlation between ν_{CT} and the ionisation potentials (electronic spectroscopic data for the CTC with CTE and photoelectronic spectroscopic data[138])

$$\nu_{CT} = (1.20 \pm 0.06)\ I_D - (6.3 \pm 0.5) \qquad (36)$$

has been established for derivatives of 11*H*-dibenzo[*b*,*f*]-azepine (XXI). The charge-transfer complexes of certain mesoionic compounds of type (XXII) have been investigated[139,140]. Analysis of the ν_{CT} data made it possible to assign the CTC of compound (XXII) with TCE to the π,π-type and to estimate the relative electron-donating capacities of the exocyclic groups in mesoionic heterocycles in the CTS.

III. PROSPECTS FOR THE APPLICATION OF THE ELECTRONIC EMISSION SPECTROSCOPY OF CHARGE-TRANSFER COMPLEXES

The application of the electronic absorption spectroscopy of the CTC to the study of intramolecular interactions is effective only on formation of comparatively stable complexes giving rise to a sufficiently intense CT band in the electron spectrum. The high sensitivity of the electronic emission spectroscopy makes it important for the study also of weak CTC. The following main applications are promising in this connection.

1. The study of the electronic emission spectra of the CTC formed in the ground state (a version which is the direct opposite of electronic absorption spectroscopy). The information thus obtained is important for the understanding of the nature of the donor–acceptor bonds[141–144]. For example, it has been shown[141,142] that the position of the CTC

emission band in the spectra of a series of benzene derivatives is determined directly by the ionisation potentials of the donors (for the same acceptor). However, overall, the electronic emission spectra of the CTC have not been as thoroughly investigated and described systematically as the electronic absorption spectra and this method has not therefore found extensive applications in physical organic chemistry.

2. Many more studies have been made (see, for example, the relevant reviews[145-147]) on the electronic emission spectra of the CTC formed only in an excited state (exciplexes) via the mechanism

$$^1D^* + A \rightleftharpoons (D^+A^-)^* \rightarrow D + A + h\nu_{CT}^{em} . \qquad (37)$$

Numerous experimental data, starting with the work of Leonhardt and Weller[148], established a linear relation between the energy of the fluorescence maximum of the exciplex $h\nu_{exc}^{fl}$, the ionisation potential of the donor I_D, and the electron affinity of the acceptor E_A similar to Eqn.(5).

Apart from these two methods, the following two indirect procedures for the investigation of weak CTC, in which the quenching of the luminescence of one of the components of the complex due to the complex formation in the excited or ground state is considered, are also important.

3. The study of the influence of the formation of non-luminescent CTC in an excited state from luminescent components. This dynamic quenching process (of the second kind[157]) corresponds to the following scheme:

$$D^* + {}^1Q \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (DQ)^* \begin{cases} \xrightarrow{k_c} {}^1D + {}^1Q & (38) \\ \xrightarrow{k_{ict}} {}^3D^* + {}^1Q & (39) \end{cases}$$

(where Q is the molecule of the quenching agent) and its kinetics are described by the familiar Stern–Volmer equation[145]:

$$\varphi_0/\varphi = 1 + k_q\tau_0[Q] = 1 + K_q[Q] , \qquad (40)$$

where ϕ_0 and ϕ are the luminescence quantum yield in the absence and presence of the quenching agent respectively, τ_0 is the lifetime of the excited state in the absence of the quenching agent (seconds), [Q] the molar concentration of the quenching agent, k_q the observed rate constant for the quenching of the luminescence (litre mol^{-1} s^{-1}), $K_q = k_q\tau_0$ the Stern–Volmer quenching constant (litre mol^{-1}), k_c the true rate constant for quenching in the complex (litre mol^{-1} s^{-1}), and k_{ict} the rate constant for the possible intersystem crossing (litre mol^{-1} s^{-1}).

For the majority of systems in solvents of low viscosity, k_q is of the order of magnitude of 10^9–10^{10} litre mol^{-1} s^{-1}, which is close to a diffusion-controlled constant $k_{dif} = 8RT/300\eta$, where R is the gas constant (J mol^{-1} K^{-1}), T the temperature (K), and η the viscosity (P). It can be shown[145] that the following relation can be derived for Scheme (38) or (39):

$$k_q = k_c k_1/(k_c + k_{-1}) . \qquad (41)$$

For strong quenching agents, $k_c \gg k_{-1}$ and we obtain

$$k_q \cong k_1 \cong k_{diff} , \qquad (42)$$

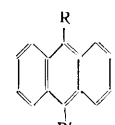
i.e. the quenching efficiency is determined exclusively by the diffusion of the species forming the intermediate complex. For a weak quenching agent ($k_c \ll k_{-1}$),

$$k_q = k_c k_1/k_{-1} = K_c k_c , \qquad (43)$$

where K_c is the equilibrium constant of the complex formation process. In this case K_q is independent of the viscosity of the solution and should be determined by the donor–acceptor properties of the fluorophor and the quenching agent.

There have been a number of studies which have confirmed this hypothesis. Thus the quenching of the fluorescence of naphthalene derivatives by carbon tetrachloride and dimethylaniline has been investigated[149]. In the first case the quenching rate constant k_q diminishes from 1.3×10^{10} litre mol^{-1} s^{-1} for 1-methoxynaphthalene to 1.3×10^7 litre mol^{-1} s^{-1} for 1-cyanonaphthalene; on the other hand, in the second case the quenching rate constant increases from 5.7×10^7 to 2.8×10^9 litre mol^{-1} s^{-1}. This indicates different donor–acceptor natures of the naphthalene derivatives: they behave as electron acceptors in the complexes with CCl_4 and as electron donors in the complexes with $NH(CH_3)_2$. Such reversal of the donor–acceptor nature of the quenching mechanism has been observed in the benzonitriles–anisoles[150] and benzophenones–substituted benzenes[151] systems.

The problem has been studied in detail in relation to the quenching of 9- or 9,10-substituted anthracenes (An) by various substances[152-155]:



(XXIII)

For the quenching of An having the general formula (XXIII) by triphenylphosphine (Pp), linear correlations have been established between the logarithm of k_q and the σ constants of the substituents, the values of ρ for compounds with electron-accepting and electron-donating substituents being 0.55 and 3.34 respectively. The positive sign of ρ shows that the quenching takes place in the complex $\overset{+}{An}Pp$ and that the quenching process is more sensitive to structural changes in the molecules for all electron-donating substituents. Analogous data have also been obtained using *N*,*N*-dimethylaniline as the acceptor. On quenching of anthracenes (XXIII) by tris(pentafluorophenyl)phosphine (PPp),[155] the opposite relation is observed: the Hammett correlations $\lg k_q \propto \sigma$ have negative reaction constants: $\rho = -1.15$ for compounds with electron-accepting substituents and $\rho = -0.78$ for compounds with electron-donating substituents. Consequently the quenching takes place via the complex $\overset{+}{An}PPp^-$. Whereas in the quenching of the naphthalene derivatives by acetyl chloride in a liquid solution the quenching efficiency (the Stern–Volmer constant) increases with decrease of the ionisation potentials of the naphthalene derivatives[158], in the quenching of polycyclichydrocarbons by tetracyanoethylene in a liquid solution the process is controlled by diffusion[159]. The quenching of the fluorescence of the acridinium ion (acceptor) by alkyl and aryl bromides and iodides (donors) probably[160] proceeds via the formation of an exciplex [see Scheme (39)], i.e. constitutes an intersystem crossing. In the case of quenching agents with ionisation potentials I_D less than 8.7 eV the process is controlled by diffusion, in accordance with Scheme (42). For $I_D > 8.7$ eV, the quenching proceeds via a charge-transfer complex, in conformity with Scheme (43). The dependence of the free energy of formation of the exciplexes on the donor–acceptor properties of the components has been examined[161,162].

4. The study of the influence of the formation of non-luminescent complexes in the ground state on the luminescence of the components:

$$^1D + {}^1Q \overset{K_c}{\rightleftarrows} {}^1(DQ) . \qquad (44)$$

For many problems in physical organic chemistry (particularly for the study of intramolecular interactions), this case (quenching of the first kind[157]) is of special interest. The literature data on this problem are extremely limited and refer mainly to liquid solutions.

According to Parker[163], quenching of the first kind is described by the Stern–Volmer equation, but the quenching constant K_Q represents the equilibrium constant of the complex formation process (44). The experimental quenching constants in this case as a rule exceed the equilibrium constants determined from the absorption spectra[164–170]. Positive deviations from the linear Stern–Volmer equation are then observed and the experimental curve is described satisfactorily by the equation[164,168–170]

$$\varphi_0/\varphi = (1+K_q[Q])(1+K_Q[Q]) \quad , \qquad (45)$$

where K_q is the constant of the dynamic quenching process (of the second kind) and K_Q is the constant of quenching of the first kind, i.e., according to Parker, the equilibrium constant for the complex formation process.

The validity of Eqn.(45) implies that two quenching mechanisms—of the first and second kinds—operate simultaneously in liquid solutions. It has been shown[170] in relation to the quenching of chlorophyll and its derivatives by aromatic nitro-compounds that the contribution of the quenching of the first kind increases as the donor–acceptor bonds are strengthened. The complex picture of the luminescence quenching process involving CTC described above hinders the application of this method to the study of weak complexes in the ground state and intramolecular interactions. However, this possibility appears when the luminescence is quenched as a consequence of the formation of complexes in the ground state in a low-temperature matrix, where the diffusion of molecules is eliminated and only the mechanism of the quenching of the first kind operates. This case has been examined in a study[171] where a linear relation between the logarithm of the Stern–Volmer quenching constant and the charge-transfer frequencies in the absorption spectra of the CTC has been found for the quenching of naphthalene derivatives by TCE at 77 K:

$$\ln K_Q \cdot 10^{-4} = -7.40\ \nu_{CT} + 14 \quad . \qquad (46)$$

In addition, a linear correlation has also been established between K_Q and K_C [the equilibrium constant of the complex formation reaction between naphthalene derivatives and TCE at 298 K (the Benesi–Hildebrand method)]:[172]

$$K_Q \cdot 10^{-4} = (2.16 \pm 0.22)\ K_c + (0.49 \pm 0.33) \quad , \qquad (47)$$

the fact that $K_Q \neq 0$ is obtained for $K_C = 0$ (the absence of complex formation in the ground state) being possibly associated with the presence of contact complexes in solution.

The method for the investigation of complex formation described above, which can be referred to as static quenching of luminescence of the first kind, can be used when (a) the linear Stern–Volmer relation holds in the working range of the concentrations of the quenching agent and (b) there is a linear relation between the logarithms of the quenching constant (or in a special case between the constants themselves) and the donor–acceptor characteristics of the substances—fluorophors or quenching agents (ionisation potentials, electron affinities, σ constants, charge-transfer frequencies, etc.). Subject to tests of the validity of the given conditions, the method has been used to investigate complex formation on the ground states of indigo–π-acceptors[173] and organometallic compounds–oxygen (or t-butyl peroxide) systems[174–176]. In the latter case valuable information was obtained about the intramolecular interactions in organomercury compounds.

* * *

Thus electronic absorption and emission spectroscopies are informative methods for the investigation of intramolecular interactions in the molecules of the species involved in charge-transfer complexes and of the characteristics of complex formation in general. The information thus obtained is important not only for the study of the mutual influence of atoms in organic and particularly organoelemental compounds (the facts concerning this field have been vigorously accumulated and treated systematically) but also for the establishment of empirical relations between the structures and reactivities of compounds and for the modelling of primary reactions in complex chemical transformations. In the latter instance, particularly for the recording of weak complexes of organoelemental compounds, emission spectroscopy in low-temperature matrices is extremely promising.

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Polyhedral Organic Molecules and Ions—Structural Analogues of Organometallic Clusters

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The results of experimental and theoretical studies are considered and the principles of the stabilisation of non-classical and highly strained polyhedral structures of organic molecules and ions are formulated. The electron count rules regulating the stability of definite polyhedral forms are analysed. The analogy between the electronic structures of organic and organometallic clusters is demonstrated.
The bibliography includes 189 references.

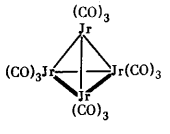
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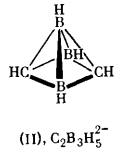
I. ORGANOMETALLIC AND HYDROCARBON CLUSTERS

Hydrocarbon chains and rings incorporating heteroatoms (oxygen, nitrogen, sulphur, etc.) as individual units make up the skeletons of organic molecules. The usual method of joining together several rings in a molecule is annelation, i.e. fusion in one plane via a common edge, while the formation of three-dimensional structures in which planar rings would correspond to individual faces of polyhedra is not characteristic of organic compounds.

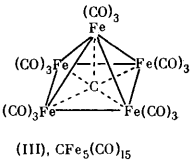
In contrast to organic chemistry, inorganic, coordination, and organometallic chemistry abound in examples of polyhedral structures: boranes, carbaboranes, transition metal carbonyl clusters, etc. Compounds (I)–(VI), chosen for illustration, comprise some of the smallest polyhedra: the tetrahedron, the tetragonal and pentagonal pyramids, the pentagonal bipyramid, and the cube.



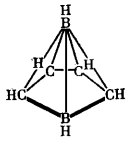
(I), $Jr_4(CO)_{12}$



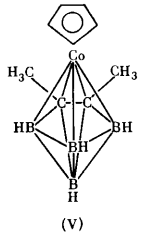
(II), $C_2B_3H_5^{2-}$



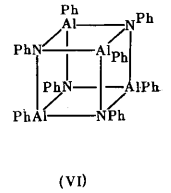
(III), $CFe_5(CO)_{15}$



(IV), $C_4B_2H_6$



(V)



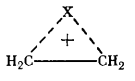
(VI)

The causes of the above difference consist in the characteristics of the electronic structures of organic and organometallic compounds. In a hydrocarbon chain or ring of an organic molecule each individual bond can be described as a two-centre two-electron bond and the number of bonding electron pairs is equal to the number of bonds, in complete agreement with the requirements of the classical theory of valence. On the other hand, in the above structures of carbaboranes and clusters the total number of valence electrons is insufficient for the formation of "normal" two-centre two-electron bonds between all the atomic centres in close proximity, which determines their classification as electron-deficient or excess-orbital compounds. However, the geometrical configurations of these compounds ensure the maximum filling of all the bonding many-centre orbitals by electrons[1–5], enabling at the same time each atom to retain around itself the number of electrons corresponding to the inert gas electronic configuration[6].

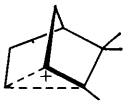
Thus, in essence, the three-dimensional structure of the molecular skeleton in electron-deficient compounds, the deviations from the standard valence angles [the bonds between carbon atoms in compounds (II)–(V)], and the unusually high coordination numbers [ranging from 5 for the carbon atom in the carbido-carbonyl cluster (III) and in the series of closo-carbaboranes[5,7] to 8 for the carbon atoms in the carbido-carbonyl clusters of cobalt and osmium[8]] are due to the necessity to observe the principal requirement of the stability of the molecular structure—the maximum utilisation of all the valence electrons for bonding. The latter becomes possible for a geometrical structure of the molecule which ensures the most effective interaction between the orbitals and its constituent fragments. The conditions for the maximum overlap of such orbitals are in general different from the requirements of the standard geometry and the usual valence limitations. The classical theory of structure and classical stereochemistry therefore lose their predictive power and the ability to describe such structures.

This fairly rare situation is encountered in organic chemistry mainly in two fields: the chemistry of non-classical ions[9] and strained structures[10]. Non-classical ions are usually understood as organic cations (electron-deficient species) containing one or more σ-bridges[9,11,12], as in the cation (VII)

or in the norbornyl cation (VIII).



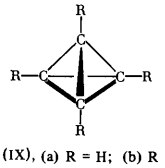
(VII), X = H, Hal, or CH_3



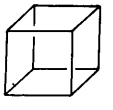
(VIII)

The enforced departure from the classical description of the cations of this type places them among the most controversial structures in organic chemistry. Thus, according to Dewar's count[13], more than 500 studies were devoted to the theoretical and experimental investigation of the norbornyl cation (VIII) as early as 1977.

In contrast to the non-classical ions, in the strained molecules, starting from cyclopropane, the standard rules of valence hold, but the valence angles are highly distorted. The compensation of the angular and bond strain necessary to ensure stability is achieved by concentrating the electron cloud within the molecular skeleton and not along the lines of individual skeletal bonds[14]. Examples of compounds of this type with regular polyhedral structures (platonic bodies) are provided by tetrahedrane (IX)[15] and cubane (X)[16].

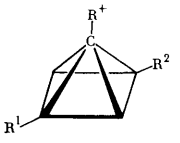


(IX), (a) R = H; (b) R = t-C_4H_9

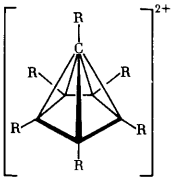


(X)

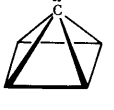
Compounds (IX) and (X) are organic analogues of clusters (I) and (VI) respectively and, like the pyramidal non-classical cations of types (XI) and (XII) obtained recently[18-20], have the same polyhedral structure as the isoelectronic *nido*-carbaboranes (II) and (IV). A pyramidal structure has been predicted by calculations[17] also for the metastable isomer of the neutral hydrocarbon C_5H_4 (XIII), whose electron deficiency is caused by the removal of the electron pair of the apical carbon from involvement in the formation of skeletal bonds.



(XI), (a) R = R^1 = R^2 = H;
(b) R = R^1 = CH_3; R^2 = H (Ref.18)
(c) R = R^1 = R^2 = CH_3 (Ref.19)



(XII), (a) R = H;
(b) R = CH_3 (Ref.20).



(XIII)

Evidently the structural similarity of the two series of compounds (I)–(IV) and (VI), on the one hand, and (IX)–(XIII) on the other, examined above, is not fortuitous and is determined by analogies between their electronic structures. Nevertheless the synthesis of compounds (IXb), (X), (XIb), and (XIIb) was treated by organic chemists as a sensation. Increasing amounts of experimental and calculated data are being accumulated nowadays on the unusual polyhedral structures of organic molecules and ions and it is becoming increasingly clear that there are common factors governing the structures of these and structurally analogous organometallic and inorganic compounds.

There is reason to believe that, from the standpoint of the nature of the chemical bond, the field of polyhedral compounds in organic chemistry is closest to organometallic and inorganic chemistry. The aims of the present review are as follows: (a) to elucidate the causes of this analogy, (b) to examine the experimental and theoretical data on polyhedral organic structures which have already accumulated, and (c) to examine the descriptive and predictive possibilities of a general qualitative approach to the study of the causes of the stabilisation of the non-classical polyhedral organic molecules and ions based on the so-called reconstruction or fragment analysis.

II. RECONSTRUCTION ANALYSIS OF THE MOLECULAR ORBITALS OF COMPLEX MOLECULES

The principal idea of reconstruction analysis is to reproduce the molecular orbitals (MO) of the entire molecule A–B–C–D–... from data for the energies and forms of the molecular orbitals of its individual fragments. This physically clear idea, which combines the simplicity and logic of classical structural representations with the quantum-mechanical description of many-centre interactions, has been used in a whole series of theoretical investigations, starting with Dewar's work[21], but has been developed most logically by Hoffmann[22,23]. His two brief reviews contain an extremely valuable bibliography on this topic.

In essence, the above problem is one of perturbation theory. Its solution at different levels of approximation has been analysed in detail[24-28]. We shall consider here briefly the most important relations for the simplest case of the interaction of two molecular fragments in terms of the one-electron approximation where the overall result of the interaction of the fragments is determined by the sum of the orbital interactions.

1. The Interaction of Fragment Orbitals

When two non-degenerate orbitals ϕ_a and ϕ_b having the energies ε_a and ε_b and belonging to fragments A and B respectively interact, two new orbitals of the overall system A–B are formed (ϕ'_a and ϕ'_b, Fig.1). The lower orbital ϕ'_a is then stabilised by the amount

$$\Delta\varepsilon_a = \frac{(H_{ab} - \varepsilon_a S_{ab})^2}{\varepsilon_a - \varepsilon_b} \quad , \qquad (1)$$

while the upper orbital ϕ'_b is destabilised by the amount

$$\Delta\varepsilon_b = \frac{(H_{ab} - \varepsilon_b S_{ab})^2}{\varepsilon_b - \varepsilon_a} \quad , \qquad (2)$$

where H_{ab} is the matrix element of the interaction operator $\langle\phi_a|H'|\phi_b\rangle$ and $S_{ab} = \langle\phi_a|\phi_b\rangle$ is the overlap integral of the orbitals ϕ_a and ϕ_b.

Like the orbital energies of the occupied and lowest unoccupied molecular orbitals, the quantity H_{ab} is negative. Since $\varepsilon_a < \varepsilon_b$ (Fig.1a), it is seen from Eqns.(1) and (2) that, in terms of absolute magnitudes, $\Delta\varepsilon_a < \Delta\varepsilon_b$. Consequently if the two orbitals of the fragments ϕ_a and ϕ_b are occupied by pairs of electrons which are transferred to the MO of the A–B system, then the overall effect of such interaction is destabilisation. The effect of the four-electron destabilisation is none other than the well known exchange repulsion of occupied electron shells. The possibility of describing this effect by Eqns.(1) and (2) depends on being able to take into account the overlap integral S_{ab} between the interacting orbitals.

A simple relation is usually postulated between H_{ab} and S_{ab}[26-28]:

$$H_{ab} = kS_{ab} \quad , \qquad (3)$$

where k varies within wide limits as a function of the method of calculation: from −8.55 eV (the Hückel molecular orbital method[26]) to −39.7 eV (the SCF MO methods[28]), etc.

Taking into account Eqn.(3), it is easy to determine which factors influence the orbital interactions. The main factor is the overlap integral between the orbitals, which is determined by the symmetry of the orbitals and their mutual orientation. The second factor is the proximity of the energy levels of the fragment orbitals. The strongest interaction corresponds to degenerate ($\varepsilon_a = \varepsilon_b = \varepsilon$) orbitals ϕ_a and ϕ_b (Fig.1*b*). In this case the stabilisation energy of the lower orbital ϕ'_a and the destabilisation energy of the upper orbital ϕ'_b of the A–B system are calculated in terms of the first-order perturbation theory with the aid of the relations

$$\Delta\varepsilon_a = \frac{H_{ab} - \varepsilon S_{ab}}{1 + S_{ab}} \quad ; \qquad (4)$$

$$\Delta\varepsilon_b = \frac{-H_{ab} + \varepsilon S_{ab}}{1 - S_{ab}} \quad . \qquad (5)$$

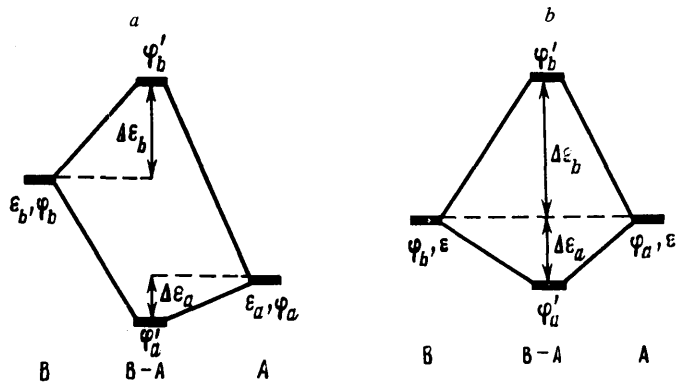


Figure 1. The formation of the MO of the A–B system (ϕ'_a, ϕ'_b) from the orbitals of the fragments A and B (ϕ_a and ϕ_b): *a*) interaction of non-degenerate orbitals; *b*) interaction of degenerate orbitals.

The orbitals of the A–B system (ϕ'_a and ϕ'_b) can be represented as a linear combination of the orbitals of the fragments A and B:

$$\varphi_a' = \varphi_a + \lambda\varphi_b \quad , \qquad (6)$$

$$\varphi_b' = \varphi_b + \mu\varphi_a \quad , \qquad (7)$$

and in absolute magnitude the coefficients λ and μ are less than unity, i.e. the orbital ϕ'_a involves a greater contribution of ϕ_a and the orbital ϕ'_b involves a greater contribution of ϕ_b. The interactions of the orbitals are additive in pairs, so that the above scheme can be readily extended to the interaction of a large number of orbitals belonging to additional fragments.

2. Fragmentation of the System. Group and Bond Orbitals

An important problem is how to isolate most effectively the fragments the interaction of the orbitals of which is most important for the determination of the stability (or instability) of the system as a whole. In the language of the LCAO-MO method, the problem is reformulated into one involving the determination of the delocalised MO of a complex system in the form of a linear combination of localised MO of its fragments, i.e. in the form of Eqns.(6) and (7).

Analysis of the wave functions and the electron distributions for a wide range of organic and inorganic compounds[29–31] has shown that, for both saturated and unsaturated and conjugated compounds, the delocalised MO can be constructed from a small number of localised group orbitals, which can be transferred from one system to another (transferable orbitals). For hydrocarbon systems, such groups are CH, CH_2, and CH_3; in the molecules with heteroatoms these are their isoelectronic fragments. Even in molecules with many-centre bonds—boranes and their derivatives[32], transition metal clusters[2,5], and π-complexes[22]—it is possible to isolate the group orbitals of several main fragments—the "building blocks" of the delocalised MO of a wide variety of compounds.

Fig.2 presents the group orbitals of the hydrocarbon fragments CH_n constructed in the form of linear combinations of the atomic orbitals of carbon (2*s*, $2p_x$, $2p_y$, $2p_z$) and hydrogen (1*s*). All the orbitals can be divided into two groups. The first includes the σ-orbitals (σ_{CH}, σ_{CH_2}, σ_{CH_3}), whose form ensures the accumulation of electron density in the region of C–H bonds. On formation of the molecule from the CH groups, these orbitals interact weakly with one another, since the overlap between them is insignificant [see Eqns.(1), (2), (4), and (5)]. Such orbitals are regarded as bonding[29]. In contrast to the group σ-orbitals, a considerable proportion of the electron density in the orbitals of the π- and *n*-types is distributed outside the range of the bonds within the groups. The interaction of such group orbitals determines the formation of new bonds and the stabilisation or destabilisation of the structure made up of several groups. The conditions for the maximum overlap of the group π- and *n*-orbitals, which depend on the relative positions of the groups, dictate the resultant geometry of the system.

We shall illustrate these postulates by analysing the MO of molecules of the type A_2H_4 formed from the group orbitals of the AH_2 fragments (Fig.3). Only group orbitals with suitable symmetry properties are combined. The nature of the stabilisation of the planar structure of C_2H_4 is related to the interaction of boundary group orbitals (*n* and *p*), leading to the formation of bonding σ_{CC} and π_{CC} orbitals of ethylene. By virtue of the considerable overlap, the interaction of the *n*- and *p*-orbitals leads to a greater splitting of their levels, the stabilisation of the bonding combination of *n*-orbitals, and the formation of bonding $\pi(1b_{1u})$-MO (lying below the atomic *p*-level).

The C_2H_4 molecule is an example of a fully occupied system of bonding MO, which is the reason for its stability in the D_{2h} configuration. For the hydrazine molecule N_2H_4, having two electrons more than the ethylene molecule, the additional electrons in the D_{2h} structure should occupy the antibonding $\pi^*(1b_{2g})$-MO. Because of this, the stable conformation of the molecule does not consist of the planar D_{2h}-form but is represented by a skewed structure (the angle of rotation about the N–N bond is ~ 90°), pyramidalised at the nitrogen atoms, in which the energetically unfavourable π*-MO is not formed[34,36].

Analysis of the scheme of orbital interactions leads to a series of general and important postulates[28,29,34,37,38], which will be used in the subsequent discussion.

(1) The main type of orbital interactions of fragments, which determines the stability of the system, is the interaction of boundary and immediately adjoining orbitals of the *n*- and π-types. The interaction of the σ-orbitals lying below is of the repulsion type but, by virtue of the small overlap of such orbitals belonging to different fragments, the repulsion effect is comparatively weak.

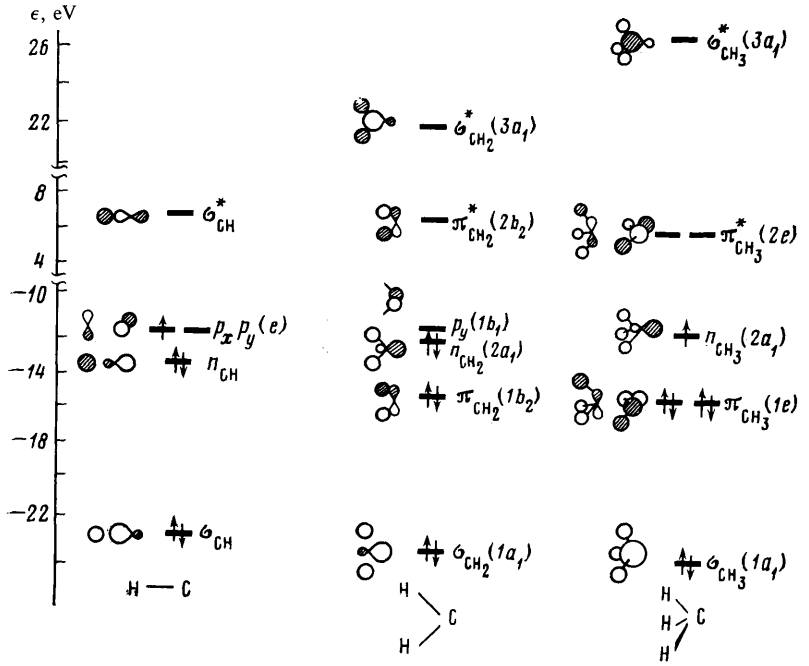


Figure 2. Group orbitals of the hydrocarbon fragments CH, CH_2, and CH_3.[29,33,34] The orbital energies have been calculated by the extended Hückel method[35].

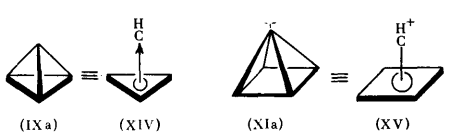
(2) Systems where the number of electrons does not exceed twice the number of bonding orbitals correspond to stable structures. This postulate constitutes the basis of all the electron count rules describing the stability of typical structures.

(3) Within the framework of the MO methods neglecting direct allowance for electron repulsions, there are no special limitations imposed on the method of fragmentation of the complex molecule or ion. However, for a qualitatively clear analysis, it is better to isolate fragments reflecting to the maximum extent the symmetry of the system and having valence orbitals of the *n*- and π-types.

3. Fragmentation of the Polyhedra

The last postulate is particularly important when the method of reconstruction analysis is applied to the determination of the MO of polyhedral structures. The structural units of the polyhedron are the vertices, edges, and faces; in a molecular system atoms or σ-linked groups, π-bonds, and conjugated cyclic fragments correspond to them. In relation to hydrocarbons, on which attention is concentrated in the present review, the vertices are C, CH, CH_2, CH_3, the edges are HC≡CH, while the faces are the $(CH)_n$ rings, where $n \geq 3$.

Pyramidal forms can be made up of these structural units by adding vertices to the basal plane, for example, via scheme (XIV) for tetrahedrane and (XV) for the cation $(CH)_5^+$.



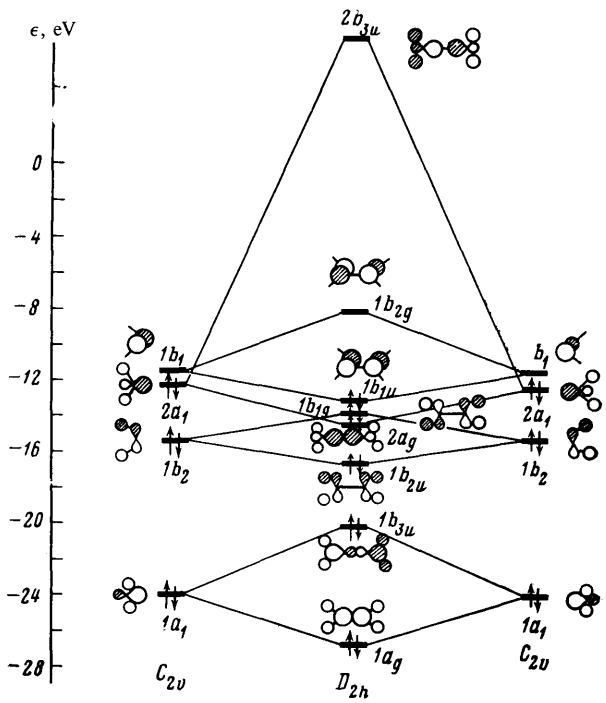
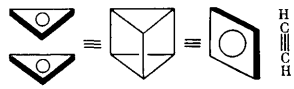


Figure 3. The formation of the MO of a molecule of the type A_2H_4 from the group MO of the AH_2 fragments. The filling with electrons for C_2H_4 and CH_2 is illustrated (calculation by the extended Hückel method).

More complex polyhedral molecules can be fragmented in several ways, using the above structural elements. Thus the prismane molecule can be made up either by the parallel superposition of two cyclopropenyl rings or by adding the acetylene edge to the cyclobutadiene ring.



This fragmentation scheme originated from the topological classification of the interactions of chains into *peri-*, *spiro-*, *longi-*, and *lati*-cyclic types developed by Goldstein and Hoffmann[39]. Indeed, although rings are absent from this scheme, they are obtained by the pericyclic combination of two or several conjugated chains (ribbons).

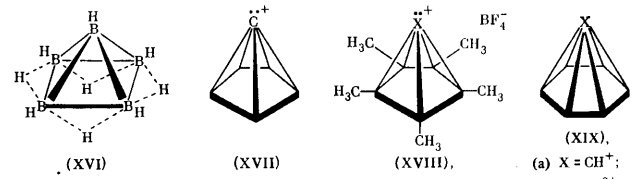
Thus, apart from the orbitals of the CH_n groups (Fig.2), the orbitals of the π-bonds (Fig.3) and those of conjugated rings $(CH)_n$ are required for the construction of the MO of polyhedral hydrocarbon structures on the basis of reconstruction analysis. The conjugated rings can be readily obtained by combining n group orbitals of CH, the full analogy between the schemes for the formation of delocalised σ- and π-MO being retained[29,30]. The different versions of the combination of the above fragments (as well as the isoelectronic heteroatomic groups) into polyhedral structures will be examined below in succession and the electronic requirements for their stability will be analysed. The results of the theoretical analysis will be compared with the results of experimental investigations.

III. PYRAMIDAL STRUCTURES

1. Pyramidal Hydrocarbons and Their Heteroanalogues

The simplest pyramidal structure is that of the tetrahedrane molecule (IXa). The problem of the synthesis of tetrahedrane was formulated more than half a century ago and stimulated a vigorous investigation of methods for the synthesis and reactions of its possible precursors[10,40]. Nevertheless the tetra-t-butyltetrahedrane (IXb) obtained recently still remains the only fairly completely characterised compound with a carbon skeleton of type (IX).[15,41] The strain energy E_{str} of the tetrahedrane molecule is 148.8 kcal mol^{-1} according to latest estimates[42], i.e. ~ 25 kcal mol^{-1} for each C–C bond, which is the upper known limit for strained organic compounds. The reason for the high value of E_{str} is evidently high angular strain.

The next member of the series of pyramidal hydrocarbons $(CH)_n$, namely the cation $(CH)_5^+$ (XIa)≡(XV) is not only a strained but also a non-classical structure with a pentacoordinate carbon atom at the vertex. The possibility of the existence of such a cation was first postulated by Williams[43], who emphasised the fact that it is isoelectronic with the pyramidal pentaborane B_5H_9 (XVI). Analysis and calculations by the extended Hückel method by Stohrer and Hoffmann[44] explained the nature of the stabilisation of this non-classical structure and almost simultaneously Masamune et al.[18] reported the experimental discovery of the dimethyl derivative (XIb), which is stable in acid media. Reactions leading to derivatives of the first pyramidal cation (XI) have been studied in detail (see the reviews[45,46] and a communication[19]) and the stability of the C_{4v} structure of the cation has been confirmed by a whole series of semiempirical[44,45,47–50] and non-empirical[51,52] calculations.

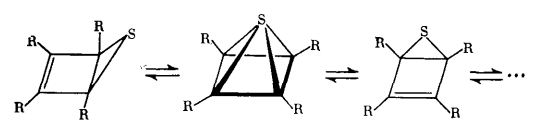


(XVI) (XVII) (XVIII), (a) X = Ge; (b) X = Sn (XIX), (a) X = CH^+; (b) X = Sn^{2+}; (c) X = Pb^{2+}.

In 1973 Hogeveen and Kwant[20,53] reported a new pyramidal C_{5v} hydrocarbon—the hexamethyl derivative of the dication $(CH)_6^{2+}$ (XIIb). An analogous pyramidal C_{5v} structure has been predicted by MINDO/3 calculations also for the metastable isomer of the cationic phenylcarbene (XVII)[54] and quite recently Jutzi et al.[55] synthesised the extremely stable germanium and tin analogues of the cationic carbene (XVIII) and demonstrated their C_{5v} structure by direct X-ray diffraction study. However, it was found that the pyramidal C_{6v} structure (XIXa), discussed as long as 20 years ago as one of the possible structures of the norbornadienyl cation[56], does not correspond to a minimum on the potential energy surface (PES) for the cation $(CH)_7^+$,[57] while the tin dication (XIXb)[58] and the lead dication (XIXc)[59] have the C_{6v} symmetry in the crystal.

The pyramidal C_{4v} structure of the hydrocarbon C_5H_4 (XIII) (pyramidane) has been shown by MINDO/3[17,60] and non-empirical[61] calculations to correspond to a fairly deep local minimum on the PES. Despite the fact that the tetracoordinate carbon atom at the apex has an extremely strained pyramidal bond configuration[62,63] (approximately sp^6 [sic.cf.Ref.62 (Ed. of Translation)] hybridisation), the strain energy per C–C bond corresponds to only 19 kcal mol^{-1}, which makes it possible to regard the synthesis of compound (XIII) as a realistic task.

The hypothesis of the formation of a pyramidal structure of type (XX) has also been put forward to account for the mechanism of the isomerisation of 2-phenylthiophen to 3-phenylthiophen[64] and of the peripheral migration of the sulphur atom in Dewar thiophen (XXI, R = CF_3)[65]:



(XXIa) (XX) (XXIb)

However calculations have shown[66] that the structure (XX, R = H) corresponds to a maximum and not a minimum on the PES for the model reaction.

The data presented make it necessary to seek an answer to the question why the existence of organic pyramidal structures (IX), (XI), (XII), (XVIII), and (XIX, b and c) is possible, while others, which should formally be formed in accordance with the same principle, cannot be realised.

2. The Eight Electron Rule

The causes of the stability of some and of the instability of other C_{nv} pyramidal structures become clear in the reconstruction analysis of the MO. Compounds with a pyramidal structure can be regarded as organic π-complexes of type (XXII) formed by the [n]annulene conjugated fragment and the apical X atom or X–R group.

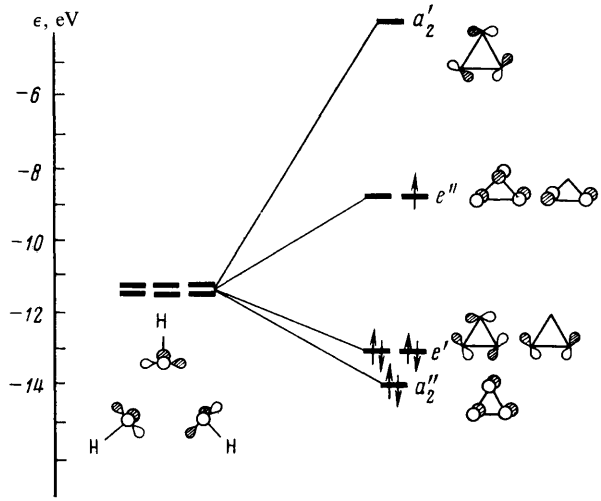
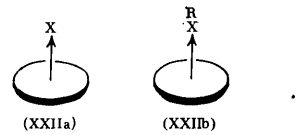


Figure 4. The formation of the MO of [3]annulene from the orbitals of three CH groups. The three p_z-orbitals of CH constitute a Hückel system and form the π-MO (a_2'', e''). The three p_y-orbitals constitute the Möbius system and form the σ-MO of the system of levels which is the inverse of that of π-MO.[67] For the complete $(CH)_3$ system, an admixture of the MO formed by the bonding CH orbitals to the molecular orbitals e' and a_2' is observed. The energies of the levels have been obtained by a calculation using the extended Hückel method.



The MO for such structures are usually constructed from the atomic or group [in the case of compound (XXIIb)] orbitals of the apical centre and the orbitals of the basal ring. The latter can be formed from the orbitals of the CH group (Fig.2) and only the MO produced by combining p-AO are capable of significant interaction with the orbitals of the apical centre, i.e. have energies close to the latter and there is adequate overlap.

Fig.4 illustrates the formation of the MO of [3]annulene from the p-AO of three CH groups. Analogous systems of π-MO and Walsh σ-MO are characteristic of any [n]annulene ring. The MO obtained by mixing the bonding σ_{CH} orbitals lie outside the valence band and their electron density is concentrated in the band of the C–H bonds[29].

Calculations have shown that, as the X, XH, or XR vertex approaches the basal ring, the overlap integrals of the valence orbitals of the above groups with the π-MO of the [n]annulene ring are greater by a factor of 3–5 than the integrals for the overlap with the Walsh σ-MO. Since the energy of the interaction of orbitals is proportional, according to Eqns.(1) and (2), to the square of the overlap integral S_{ab}^2, it follows that in a qualitative study it is sufficient to take into account only the interaction between π-MO of the basal ring.

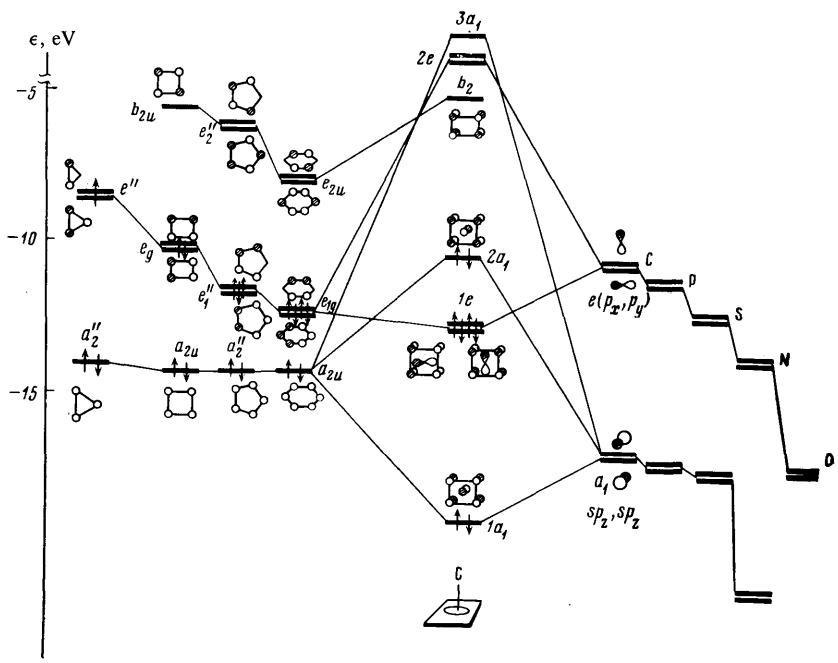
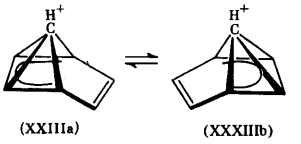


Figure 5. The reconstruction analysis of the MO of C_{nv} pyramidal systems formed by the [n]annulene ring and the apical atomic centre. The molecule of pyramidane has been chosen as an example. The MO energies have been calculated by the extended Hückel method; the energies of the hybrid orbitals were taken from Hinze and Jaffé.[68] For the C_{4v} and C_{5v} structures with an apical atom more electronegative than phosphorus and for all C_{3v} structures, an inversion of the $1e$ and $2a_1$ levels is observed.

We shall consider initially pyramidal structures of type (XXIIa) to which compounds (XIII), (XVII), (XVIII), and (XX) belong. The valence orbitals of the apical atom can be conveniently regarded as a pair of hybrid sp_z-orbitals and a pair of p_x- and p_y-orbitals. Fig.5 presents a generalised[17, 54,55,66,69] correlation diagram for the C_{nv} pyramidal system (XXIIa). The interaction of the lowest π-orbital of annulene with a pair of hybrid orbitals of the apical atom, having identical symmetry properties, leads to the formation of the bonding ($1a_1$), non-bonding ($2a_1$), and antibonding ($3a_1$) MO. Since the initial fragment orbitals are completely filled with electrons, the resulting effect of this orbital interaction is destabilisation. The fragments are bound together as a consequence of the mixing of the lowest e-MO of the ring with the p-AO of the apical atom and the formation of the bonding $1e$-level of the C_{nv} pyramidal system.

Thus the orbital interactions of the fragments of any C_{nv} pyramidal structure described above give rise to three bonding and one non-bonding MO, which can accommodate eight electrons. If the number of π-electrons of the basal ring and of the valence electrons of the apical centre (it has been suggested[70] that these electrons be referred to as "inner") exceeds eight, the antibonding MO is filled, which destabilises the structure. Indeed the hypothetical structures of pyramidane (XIII), the cationic carbene (XVII), as well as compounds (XVIII) and (XIX, b and c) meet the above requirement, whereas the C_{4v} structure (XX) and the C_{6v} structure (XIXa) each contain 10 inner electrons and do not actually occur. In order to become adapted to the requirement of an eight-electron shell, such structures are distorted to give less symmetrical forms: (XXIa) for thiophen and (XXIII) for the norbornadienyl cation, for which the fluctuating conformation with a single "disconnected" π-bond is stable[71,72].



(XXIIIa) (XXXIIIb)

The correlation diagrams for pyramidal structures of type (XXIIb)[44,46,70] are analogous to that presented in Fig.5, which is due to the similarity of the fragment orbitals. Fig.6 illustrates the relation between the structure of the MO of the (XXIIa) and (XXIIb) systems. The significant difference is that the non-bonding $2a_1$ level in structures (XXIIa) is transformed into the low-lying $1a_1$ level of the X–R bond, which stabilises the structure. Like structure (XXIIa), structures (XXIIb) contain four bonding MO, which can be filled by not more than eight electrons, including the π-electrons of the basal ring, the valence electrons of the atom X, and one additional electron from the group R involved in the formation of the electron pair of the X–R σ-bond.

In combination with the analogous conclusion for compounds (XXIIa), the above conclusion can be regarded as the formulation of the eight electron ($8e$) rule for the stability of C_{nv} pyramidal structures. The $8e$ rule can be understood as the tendency of the apical atom of the non-transition element to build up its electron shell to that of the corresponding inert gas. In this sense, it is analogous to the familiar 18 electron rule for transition elements.

Taking into account the $8e$ rule, it is possible to postulate the capacity for the existence of pyramidal organic molecules and ions of types (XXIV) and (XXV).

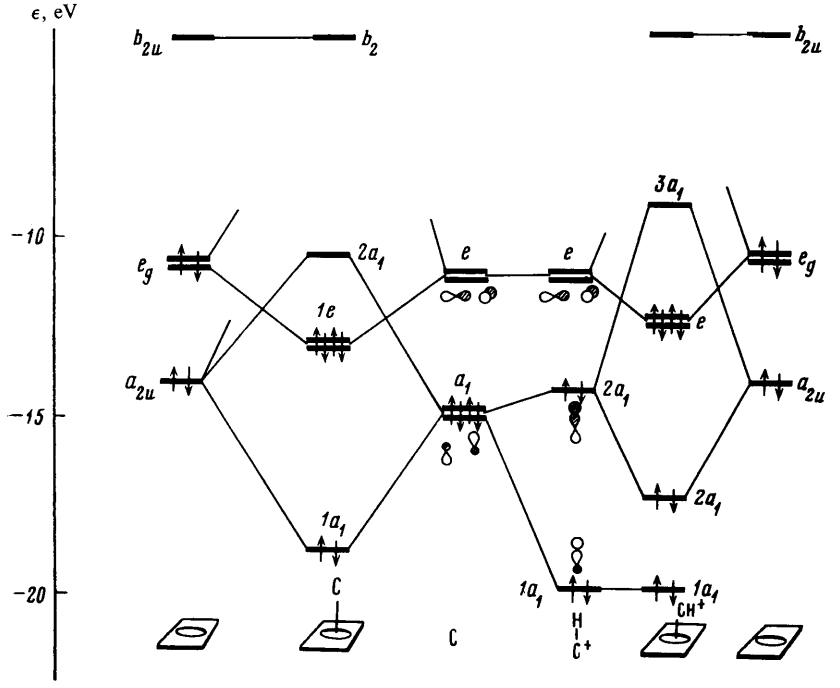
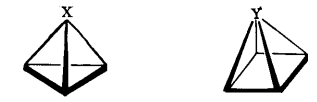
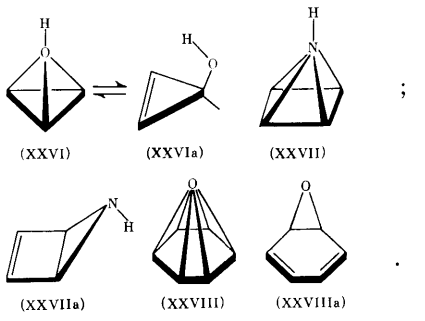


Figure 6. Relation between the correlation diagrams for the MO of the pyramidal structures (XXIIa) and (XXIIb). Pyramidane and the $(CH)_5^+$ cation have been chosen as examples.



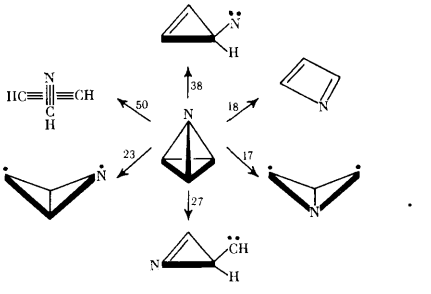
(XXIV), X = C⁻, CH, N, P, O⁺, or S⁺ (XXV), Y = C, CH⁺, Si, SiH⁺, N⁺, P⁺, O²⁺, or S²⁺ .

Calculations[69,73] by the MINDO/3 method with complete optimisation of all the geometrical parameters have indeed shown that all the structures quoted above for the C_{3v} and C_{4v} symmetry correspond to local minima on the PES. On the other hand, the non-classical structures (XXVI)–(XXVIII), which do not satisfy the 8*e* rule, correspond to maxima on the PES and relax to the stable forms (XXVIa)–(XXVIIIa):

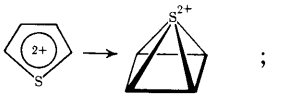


(XXVI) (XXVIa) (XXVII) ; (XXVIIa) (XXVIII) (XXVIIIa) .

The validity of the 8*e* rule implies merely that the structure corresponds to a minimum on the PES for a molecule or ion. In order that such a structure should have a sufficiently long lifetime, it is necessary that it should have adequate kinetic stability in relation to different possible isomerisation and ring decomposition reactions. Detailed non-empirical[74] and MINDO/3[75] calculations on such transformations have been made for the tetrahedrane molecule, which is kinetically stable despite its strain. The pyramidane molecule has analogous properties[76]. The above schematic formulation[69] of the ring decomposition and isomerisation reactions involving another hitherto unknown pyramidal structure, namely that of azatetrahedrane (XXIV, X = N), where the numerals above the arrows indicate the activation barriers (kcal mol^{-1}) calculated by the MINDO/3 method, also indicates the kinetic stability of this compound even in relation to more stable isomers {azacyclobutadiene, 3-azabicyclobutane[1.1.0]diyl} and the decomposition products:



On the basis of the rule formulated above, it is possible to predict transformations which should lead to non-classical pyramidal structures. Non-empirical and MINDO/3 calculations[77] suggest that the thiophen dication (XXIX) is unstable and relaxes without an activation barrier to the pyramidal dication (XXV, Y = S^{2+}):

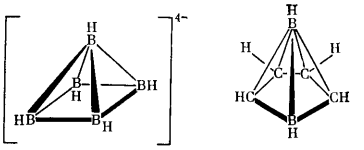


(XXIX) (XXV), Y = S^{2+} .

3. Pyramidal Structures in a Series of Boranes and Organometallic Compounds of Non-transition Metals

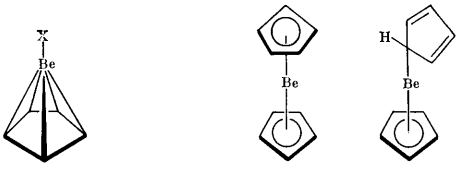
In contrast to organic compounds, the pyramidal (*nido*) structures are not an exception but the rule in the series of boranes and carbaboranes[1,4,7,78]. Electron count rules, taking into account the so-called skeletal electrons of all the groups[2–5], which are discussed above (see Section VI) have also been developed for these compounds. The 8*e* rule constitutes an equivalent formulation.

On the basis of the fragmentation scheme examined above, Lipscomb[1] predicted that the $B_nH_n^{4-}$ anions should have the pyramidal *nido*-structure, for example, compound (XXX, $n = 5$). Indeed the sum of the π-electrons of the basal ring (0) and the electrons of the apical group (8) is 8. The pyramidal structure (II) is expected[4] for the dianion $C_2B_3H_5^{2-}$ (2 + 6 inner electrons), isoelectronic with compound (XXX). For the stable *nido*-carbaborane $C_4B_2H_6$ (XXXI), this structure has been established experimentally[7,79] (4 + 4 inner electrons). In general any carbaboranes $C_4B_{n-4}H_n$ and the dianions $C_2B_{n-2}H_n$ should have the $C_{(n-1)v}$ pyramidal *nido*-structure:



(XXX) (XXXI) .

Numerous pyramidal C_{5v} structures have been found for derivatives of cyclopentadienylberyllium hydride (XXXII). Data on the structures of and theoretical calculations for these compounds have been described[70,80]. The beryllocene molecule (XXIII), whose structure has been investigated by all possible experimental methods, including electron diffraction and low-temperature X-ray diffraction measurements[31,81–83], is of special interest in this series. The sandwich structure (XXXIIIa) and the half-sandwich structure (XXXIIIb) are believed to be most probable. The latter belongs to type (XXIIb) and corresponds to the 8*e* rule, to which Jemmis et al.[80] relate the results of their calculations (STO-3G basis set), indicating that structure (XXXIIIb) is preferable. Recent more complete calculations[82] using an extended basis set led to an analogous conclusion. It is of interest that the structure of the MO of the valence band obtained in this calculation is exactly consistent with the qualitative scheme in Fig. 6.



(XXXII), (a) X = H, (b) X = CH_3, (c) X = BH_4, (d) X = Cl, (e) X = Br (XXXIIIa) (XXXIIIb) .

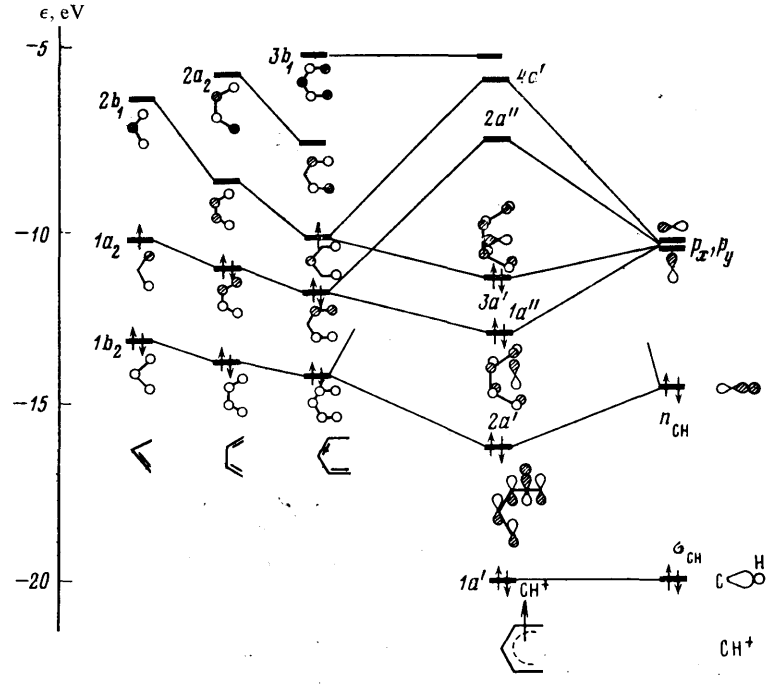
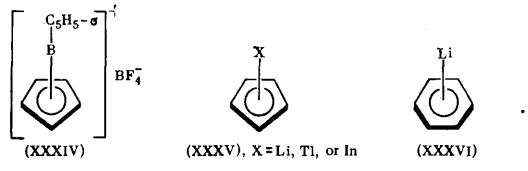


Figure 7. Reconstruction analysis of the MO of the non-classical cations formed by a polyene chain and a CH^+ vertex. The cation (XXXVIII) has been taken as an example. The MO energies have been calculated by the extended Hückel method.

A pyramidal structure has been established by X-ray diffraction for the cation (XXXIV), which is isoelectronic with beryllocene[84]. Cyclopentadienylthallium[85] and cyclopentadienylindium[86] have analogous structures in the gas phase (8 inner electrons). According to calculations[87,88], cyclopentadienyl-lithium also has the C_{5v} structure (XXXV). The number of inner electrons in this compound is 6, which leads to additional stabilisation, since the non-bonding $2a_1$ MO (Fig.5) remains unoccupied. Presumably, in conformity with the 8*e* rule, the stable form of cycloheptatrienyl-lithium has the pyramidal C_{7v} structure (XXXVI):

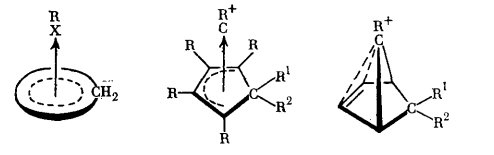


(XXXIV) (XXXV), X = Li, Tl, or In (XXXVI)

4. Homoconjugated Rings in the Basal Plane

Cyclic groups produced by the insertion of methylene and isoelectronic groups in one or several bonds of the [*n*]annulene ring also have a system of π-orbitals suitable for effective binding to the apical group. Such substitution diminishes but does not abolish the endocyclic orbital interactions and, according to a theorem[39], the symmetry of the π-orbitals in such a ring does not change compared with the initial conjugated ring. Consequently the type of interaction of these orbitals with those of the apical fragment does not change and the 8*e* rule can be extended to pyramidal structures, in the basal plane of which there is a polyene group, isolated π-bonds, and individual π-centres, the relative disposition of which is close to that of a closed ring.

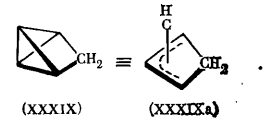
Fig.7 illustrates the formation of four bonding MO in structures of type (XXXVII) in relation to the homo-$(CH)_5^+$ cation (XXXVIII):



(XXXVII) (XXXVIII) (XXXVIIIa)

In contrast to the C_{nv} pyramidal systems (XXIIb), the structures (XXXVII) have only a plane of symmetry and the apical centre is not equidistant from all the π-centres coordinated to it. The latter follows from ^{13}C NMR data for a series of hexamethylbicyclo[2.1.1]hexenyl cations (XXXVIII, R = CH_3)[45,46] and has been confirmed by MINDO/3 calculations[19].

The structure of the molecule of homotetrahedrane (XXXIX), which has been recently synthesised[40], can also be represented by analogy with scheme (XXXVII) as one involving the stabilising interaction of the 3π-electron allyl fragment with a 5-electron group CH [structure (XXXIXa)]:

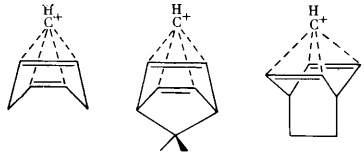


(XXXIX) (XXXIXa)

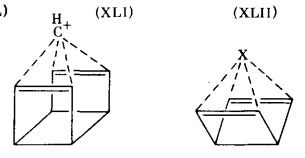
The form of the MO of the polyene chain (Fig.7) explained satisfactorily the asymmetrical orientation of the apical group X. Thus the displacement of this group towards the centre of the allyl fragment in compound (XXXIXa) and conversely towards the terminal atoms of the butadiene fragment in

compound (XXXVIII) is determined by the conditions for the maximum overlap of the interacting orbitals of the polyene and apical centre.

The bishomo-$(CH)_5$ cation (XL)[45,89] and a series of derivatives of the cations (XLI)[90–92] and (XLII)[93] have been synthesised from suitable precursors and have been studied in detail. Calculations on compounds (XL)[45] by the MINDO/2 method and on compounds (XLI)[50] and (XLIII)[94] by the MINDO/3 method demonstrated their high kinetic stability in relation to various rearrangements. It has been shown by the same computational procedure that structures (XL)–(XLIII), containing at their vertices other four-electron groups instead of CH^+, as well as structure (XLIV) correspond to the minima on their PES.[95]

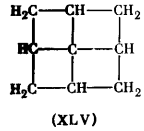


(XL) (XLI) (XLII)



(XLIII) (XLIV), X = CH^+, C, or N^+

The polyhomopyramidal structures are unusual. Compound (XLV), which has been called[96] fenestrane (from the latin fenestra = window), containing the tetrahomocyclobutadiene ring on the periphery, has attracted special attention in connection with the possibility of a sterically constrained planar configuration, or a configuration flattened to the maximum extent, of its central tetracoordinate carbon atom[10,97,98]. MINDO/3 calculations[99] have shown that two conformations of fenestrane, with flattened tetrahedral (XLVa) and pyramidal (XLVb) configurations of the central carbon, are possible. The basis set of orbitals in the pyramidal conformation (XLVc) is topologically equivalent to that of pyramidane.



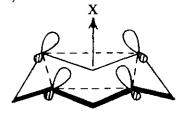
(XLV)



(XLVa), ΔH_f = 108.5 kcal mol^{-1}; S_4

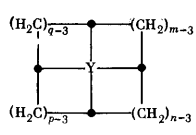


(XLVb), ΔH_f = 137.8 kcal mol^{-1}; C_{4v}

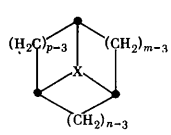


(XLVc)

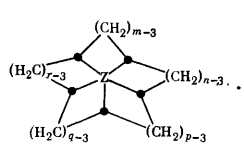
According to Greenberg and Liebman[10,100], compounds (XLV) can be regarded as members of the general series of [*m.n.p.q*] fenestranes (XLVI), i.e. [4.4.4.4]fenestranes. It has been suggested[99] that the definition of fenestranes be extended to *n*-gonal "windows" in such a way that compounds of types (XLVII) and (XLVIII) can be defined as [*m.n.p*]fenestranes and [*m.n.p.q.r*]fenestranes:



(XLVI, Y = CH^+, C, N^+, or S^{2+})



(XLVII, X = CH, or N)

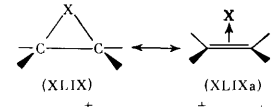


(XLVIII, Z = B, BeH, or CH^{2+})

The validity of the 8*e* rule for the (XLVI)–(XLVIII) system has been confirmed by direct MINDO/3 calculations with optimisation of the geometry[99,101]. It is noteworthy that the series of fenestranes defined in the above manner includes as the initial members tetrahedrane as [3.3.3]fenestrane, pyramidane as [3.3.3.3]fenestrane, and the dication (XII) as [3.3.3.3.3]fenestrane, which were discussed above.

5. Three-membered Rings–Apex above the π-Bond

When the size of the polyene chain in compound (XXXVII) or of the basal ring in compound (XXII) is reduced to the limiting extent, it is possible to arrive at a two-dimensional version of the interaction of the apex and the π-bond, i.e. the three-membered ring (XLIX). In view of the large deviations from the normal valence angles, structures of this type are highly strained and the usual ideas concerning the nature of the bonding reflect inadequately the characteristics of their electronic structure:



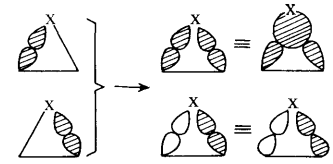
(XLIX) (XLIXa)

X = CH_2, CH_3^+, BH_3, NH, NH_2^+, O, OH^+, S, SH^+, F^+, Cl, or Ag^+.

In this connection Walsh[102] stated as early as 1947 that the structures of cyclopropane (X = CH_2), oxiran (X = O), and other compounds of type (XLIX) correspond to the π-complexes (XLIXa). The MO of these compounds were first described by Dewar[103], who recently examined in detail the genesis and evolution of the ideas in this field[104].

The correlation diagrams in Fig. 8 illustrate the mechanism of the binding of the fragments of the molecules of compounds (XLIX) in relation to oxiran and thi-iran (X = O or S). The stabilisation is due to the effect of the $\pi \rightarrow p_z$ and $p_x \rightarrow \pi^*$ interactions, referred to respectively as direct and reverse donation. The ratio of the contributions of these interactions depends on the relative positions of the levels of these orbitals, i.e. on the electronegativity of the atom X. When the electronegativity of X is high, as in the case where X = O, the difference between the energies of the *p*- and π*-orbitals is large and the orbital interaction is weak [see Eqns. (1) and (2)]. In Fig. 8 this is reflected by the slight changes in the form of the fragment orbitals in the oxiran MO $1b_2$ and $2b_2$, in conformity with Eqns. (6) and (7). In three-membered rings of this type the reverse donation effect is small and these structures qualify, in terms of the adopted terminology, as π-complexes. In the case of thi-iran the lower electronegativity of the sulphur atom is responsible for the comparable magnitudes of the direct and reverse donation effects. It has been suggested that such compounds be regarded as[104] normal three-membered rings.

Such subdivision is naturally extremely arbitrary, which is clear from a simple argument[105]. Symmetrised combinations (Lb) of the orbitals of two X–C σ-bonds of structure (XLIX) (normal three-membered ring) constitute none other than two bonding MO $2a_1$ and $1b_2$ (Lc), corresponding to the forward and reverse donation in the π-complex model (Fig. 8):



(La) (Lb) (Lc)

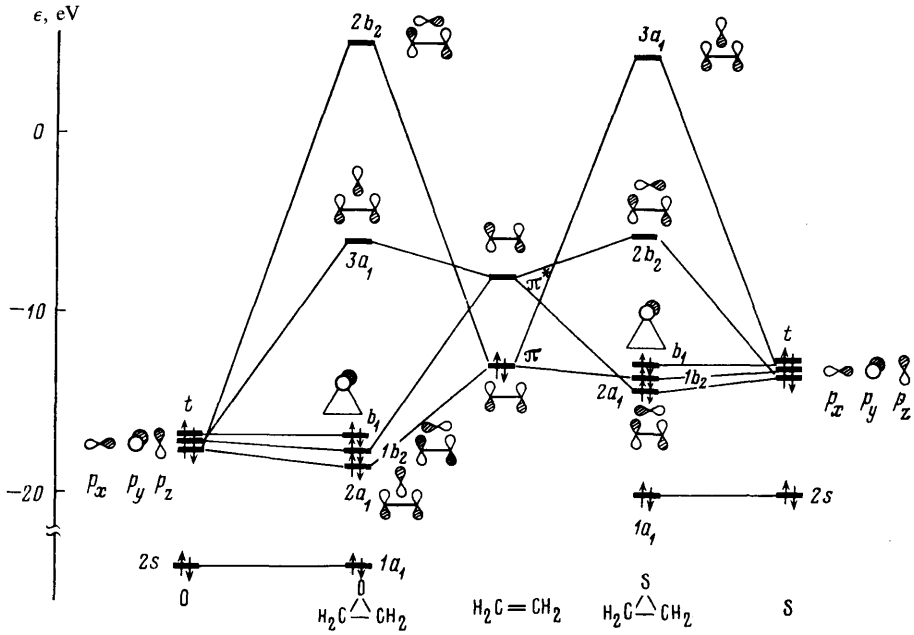


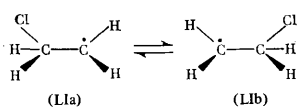
Figure 8. Correlation diagram for the MO of compounds (XLIX, X = O or S). In view of the high electronegativity of oxygen the $p \rightarrow \pi^*$ back-donation in epoxyethane is insignificant.

The significance of the above subdivision consists in the fact that it emphasises the ratio of the contributions of the forward and reverse donation, i.e. the stabilisations of the MO $2a_1$ and $1b_2$, and makes it possible to relate this ratio to the geometrical features and the reactivities of compounds (XLIX). The following series of groups X, in which the π-complex character of compounds (XLIX) diminishes, has been proposed[104]:

$$H^+ > SiH_3^+ > P^+ > CH_3^+ > Cl^+ > OH^+ \sim SH^+ \sim$$
$$\sim O \sim NH_2^+ \sim NH \sim PH_2^+ \sim S > CH_2 \sim PH > SiH_2 .$$

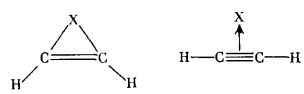
It follows from the correlation diagram in Fig.8 that the 8*e* rule should hold for the "pyramidal" structures (XLIX). Consequently, local minima on the PES should correspond to structures satisfying this rule. Indeed the stable cyclic cations (XLIX) with X = RS^+,[106,107] Cl^+,[108,109] and RO^+[110] have been discovered experimentally. A whole series of studies have been made[104,111–115] on calculations of their electronic and steric structures. The cation (XLIX, X = F^+), in which the $p \rightarrow \pi^*$ interaction is very weak, has aroused particular controversy. Nevertheless non-empirical calculations[111] and MINDO calculations with a detailed specification of the location of the stationary points on the PES[114] demonstrated the presence of a minimum for the cyclic form, located 10.3 kcal mol^{-1} (STO-3G) or 18.7 kcal mol^{-1} (MINDO) above the minimum for the 2-fluoroethyl cation $FCH_2CH_2^+$.

The introduction of additional electrons into the highly antibonding MO $2b_2$ (Fig.8) destabilises sharply the cyclic structure. Thus the radical (LI) is incapable of existing in the cyclic form (XLIX, X = Cl)[116] and the corresponding anion totally decomposes into ethylene and the chloride ion[117]:



(LIa) (LIb)

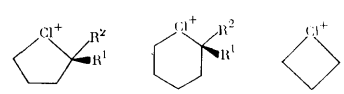
On the basis of the orbital interactions of the fragments of compound (XLIXa), it is possible to understand also the secondary characteristics of the structure: the rehybridisation of the basal atoms and the displacement of the O–H, B–H, and N–H bonds from the plane of the ring. The σ-orbitals of the above bond are then included in the interaction with the non-bonding MO b_1 of the ring (Fig.8). This orbital forms an overall closed π-system with the π_4-MO of the acetylenic fragment in the three-membered rings (LII):



(LII) (LIIa)

For X = O or S, this system is antiaromatic, which constitutes a powerful destabilising factor. Nevertheless, the extremely unstable compounds oxirene (X = O)[118,119] and thi-irene (X = S)[120] have been discovered experimentally.

The separation of the π-centres of the basal bond, i.e. transition to groups of the type $H_2C-(CH_2)_n-CH_2$, does not alter the form of the boundary orbitals. Olah[121,122] demonstrated the existence in solution of the stable cyclic halogenonium ions (LIII, *a* and *b*):



(LIIIa) (LIIIb) (LIIIc)

Theoretical and experimental study of the ion (LIIIa) demonstrated the high stability of the cyclic form relative to the classical open-chain isomer[123]. An analogous result has been obtained in calculations[124] for chloronium ions (LIII, *b* and *c*).

IV. SANDWICH STRUCTURES

Compounds of the sandwich type (LIV), the first representative of which was ferrocene (LV, M = Fe), discovered in 1951, constitute the most important type of organometallic compounds of transition elements[125]. However, analogous compounds of the non-transition elements in Periods II and III are unknown.

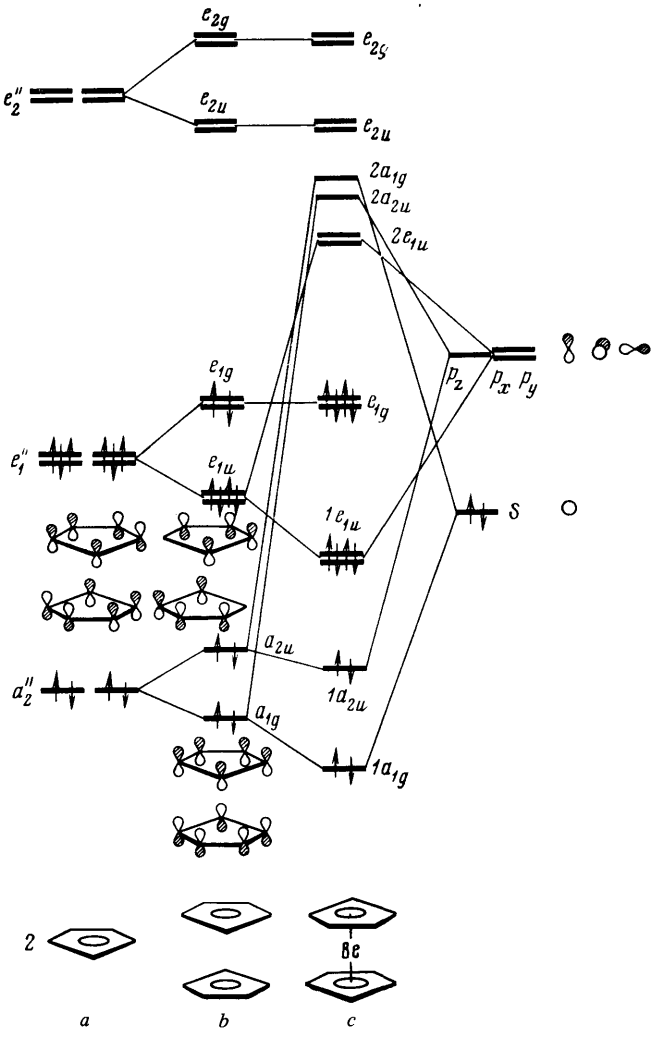
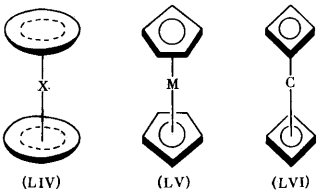


Figure 9. Correlation diagram for the MO of the beryllocene molecule in the sandwich form (D_{5d} symmetry) according to Jemmis et al.[80]: *a*) MO of two non-interacting cyclopentadienyl fragments; *b*) the splitting of the MO of the cyclopentadienyl rings which have approached one another to the equilibrium distance; *c*) MO of the structure (XXXIIa). Only the bonding combinations of the orbitals of the two cyclopentadienyl rings which have approached one another are shown.

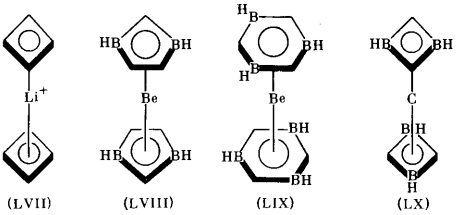
As already mentioned, the sandwich structure (XXXIIa) ≡ (LV) has not been confirmed for beryllocene (M = Be) in the light of the latest investigations:



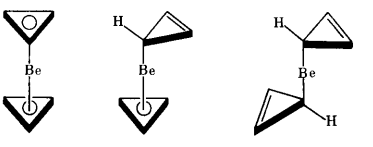
(LIV) (LV) (LVI)

The causes of this are the rigid electronic limitations for structures (LIV): the sandwich structures of compounds of non-transition elements must contain in the π-orbitals of the cyclic fragments and in the valence orbitals of the central atom not more than eight electrons[70]. This conclusion can be clarified by the reconstruction analysis of the MO of the sandwich compound (LV) (Fig.9).

Only four bonding MO orbitals can be formed by the fragment orbitals of compound (LIV) in both D_{nd} and D_{nn} geometry. Since there are 12 "inner" electrons in the biscyclopentadienylberyllium sandwich, this structure is unstable. For another 12-electron structure, namely that of the hypothetical hydrocarbon bis(η^4-cyclobutadienyl)carbon (LVI), the strain energy calculated by the MINDO/3 method is 31 kcal mol^{-1} for each C–C bond[126], which is much higher than the values for tetrahedrane and pyramidane. On the other hand, structures (LVII)–(LIX)[70] and (LX)[126], which satisfy the requirement of the 8*e* rule for sandwich structures, can be stable. Thus the calculated heat of formation of compound (LX) is −7 kcal mol^{-1} against 476 kcal mol^{-1} for compound (LVI).



When the approaches to sandwich structures (LIV) are considered, one must bear in mind that, even when the requirements of the 8*e* rule are met, an alternative to the pyramidal form exists for the majority of them, as in the case of biscyclopropylideneberyllium (LXI). Calculations[70] have shown that structure (LXIb) is preferable to structure (LXIa), but the bis(η'-cyclopropylidene) form (LXIc) is energetically most favourable. The cause of this tendency is determined by the fact that, although the *e*″-MO of [3]annulenes are in fact stabilised by the interactions with the central atom in the π-complex, nevertheless a strong antibonding character is retained within the ring (Fig.5), which is eliminated in structure (LXIc). The important role of this factor in the analysis of the stability of sandwich structures in relation to various fragmentations was pointed out for the first time by Lopatko et al.[127]



(LXIa) (LXIb) (LXIc)

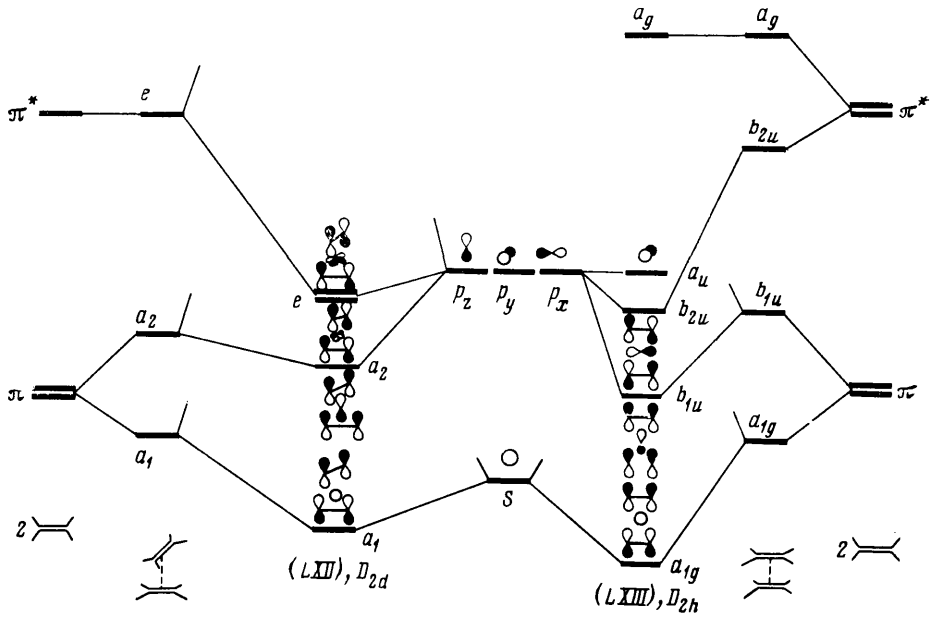
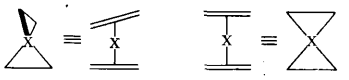


Figure 10. Correlation diagram for the MO of the orthogonal and planar spirorings (LXII) and (LXIII). The bonding MO are shown.

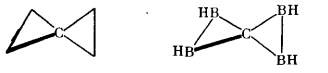
The spirocyclic compounds (LXII) can be regarded as a special case of sandwich structures. The structural alternatives—D_{nd} or D_{nh} symmetry[125,128]—usual for sandwich compounds (LIV) reduce in the given instance to a choice between orthogonal and coplanar dispositions of the multiple bonds of the fragments:



(LXII) (LXIIa) (LXIIIa) (LXIII)

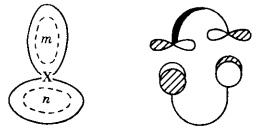
It is clear from the correlation diagram in Fig.10 that the orthogonal structure (LXII) is preferable, since the p_y-orbital of the central atom in compound (LXIII) remains isolated. The structure of the MO in compound (LXII) is analogous to that of compound (LIV) (Figs.9 and 10). The bonding MO of structure (LXII) accommodate 8 electrons, i.e. spirans with a four-electron central atom (C, N^+) are stable, whereas the stabilisation of the planar structure (LXIII) requires a two-electron centre (Be, B^+).

Another version of the stabilisation of a planar spiran involves the replacement of the carbon atoms and the nodes of the ethylene fragments by boron atoms. This approach to the problem of the stabilisation of a planar tetracoordinate carbon atom was put forward by Hoffmann[129] and developed by Schleyer, Pople, and coworkers[98,130]. As an example, we present the differences between the energies of the planar and orthogonal conformations of spiropentane (LXIV) and tetraboraspiropentane (LXV) obtained in non-empirical calculations (STO-3G and 4-31G basis sets):



(LXIV), ΔE = 167 kcal mol^{-1} (LXV), ΔE = 6 kcal mol^{-1}

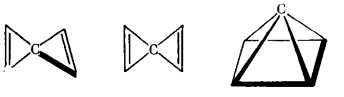
The spirans (LXII) can be formally regarded as the first members of the series of spirarenes (LXVI) with even m and n[131,132]. The main type of orbital interaction in such systems involves the overlap of antisymmetric orbitals (LXVII).



(LXVI) (LXVII)

The stabilisation of $[m,n]$spirarenes with odd m and n is achieved if the following electron count rule is obeyed: m and n must be equal to $4q + 3$, where $q = 0,1,2,...$[39,132]. The theory of spiro-conjugation and the experimental consequences of this effect have been examined in reviews[132,133].

Orbital interactions of type (LXVII) occur in addition to $p-\pi$ interactions in spirans of type (LXII) where the double bonds have been replaced by triple bonds. The spiropentadiene (LXVIII), for which the isomerisation PES has been investigated by the MINDO/3 and extended Hückel methods, constitutes an interesting case[17]. It has been found that the planar D_{2h} form (LXVIIIa) corresponds to the transition state (57 kcal mol^{-1}) in topomerisation via a diagonal twist mechanism; PES contains a second minimum, whose depth is smaller than that of the minimum corresponding to structure (LXVIII) by only 14 kcal mol^{-1} and which corresponds to the structure of pyramidane (LXVIIIb) = (XIII).



(LXVIII) (LXVIIIa) (LXVIIIb) ≡ (XIII)

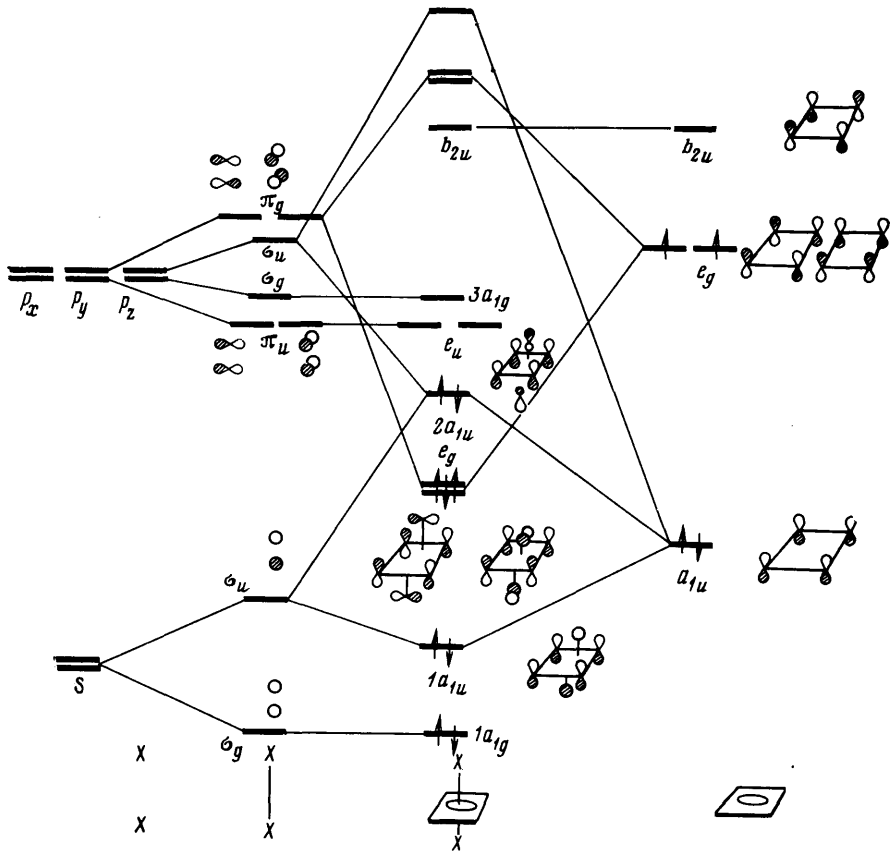
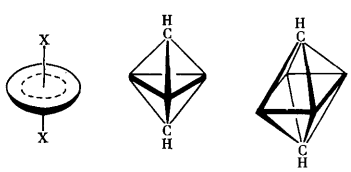


Figure 11. Correlation diagram for the MO of bipyramidal D_{nh} structures (LXIX)[69]. The D_{4h} structure has been adopted as an example.

V. BIPYRAMIDAL STRUCTURES

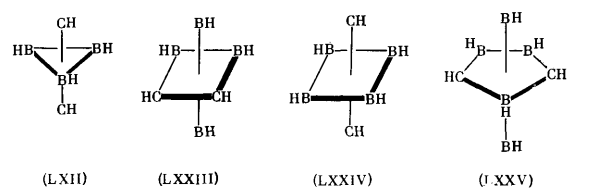
The addition of yet another vertex to the pyramid entails the formation of bipyramidal structures (LXIX) (inverted sandwiches).



(LXIX) (LXX) (LXXI)

In their study of the cation $(CH)_5^+$, Stohrer and Hoffmann[44] already discussed the trigonally bipyramidal D_{3h} form (LXX) and found it to be less favourable than the pyramidal C_{4v} structure (XIa). MINDO/3 calculations[46] showed that the energy difference reached is 100 kcal mol^{-1} and, what is most important, structure (LXX) does not have the properties of a local minimum in the PES of $(CH)_5^+$. The D_{3h} form of the anion $(CH)_5^-$ does not have these properties either[134]. Formally the D_{4h} structure (LXXI) of $(CH)_6$, isomeric with benzene, contains six pentacoordinate carbon atoms. Non-empirical calculations[135,136] indicate an extreme instability.

The unusual valence states of the carbon atoms in compounds (LXX) and (LXXI) are not, however, the main reason for their instability, since the replacement of some of their CH vertices by BH gives rise to stable bipyramidal *closo*-carbaboranes $C_2B_{n-2}H_n$,[2,4,7] for example:



(LXII) (LXXIII) (LXXIV) (LXXV)

We shall consider the electronic requirements which must be met by the stable bipyramidal structure. Fig.11 shows that only those combinations of the orbitals of apical centres can interact with the π-MO of the central ring which are antisymmetric in relation to its plane. The lowest π-MO a_{1u} produces on interaction with $\sigma_u(s)$- and $\sigma_u(p_z)$-orbitals the bonding ($1a_{1u}$), non-bonding ($2a_{1u}$), and antibonding molecular orbitals of the pyramidal structure, of which the first two are stabilised. Two π_g-orbitals of the apical centres give rise to a further two stabilised MO on interaction with the e_g-MO of the ring. Instead of the $\sigma_g(s)$-combination, it is possible to isolate five stabilised MO, which ensure bonding between the central ring and the pair of apical centres. They can be populated by not more than 10 electrons (counting the π-electrons in the ring and the valence electrons of both apices), which constitutes the 10*e* rule for the stability of bipyramidal structures (LXIX)[69].

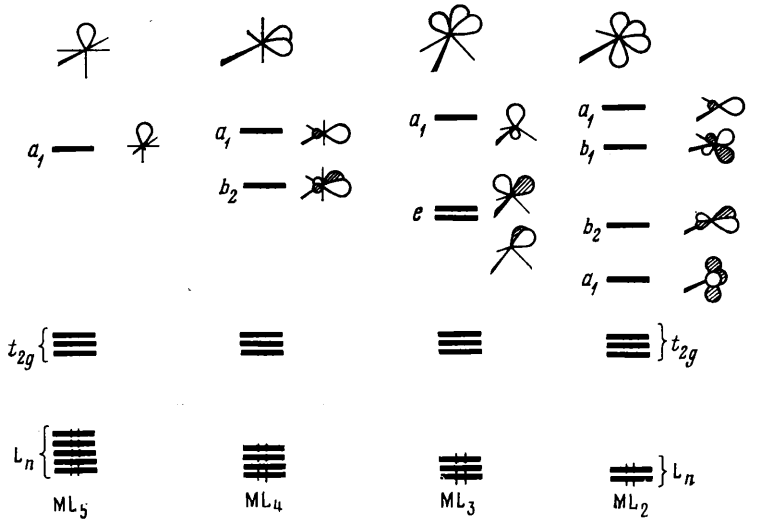


Figure 12. The group orbitals of the ML_n fragments in which M is an atom of a transition element and L are two-electron ligands (CO, Cl, PX_3, etc.). The analytical functions of the MO have been published[144,145]. The a_1 and b_2 levels for ML_n and a_1 and e for ML_3 are inverted relative to the corresponding levels of the CH_2 and CH groups (Fig.2) owing to the contributions of the d-orbitals to the group MO of ML_n and the changes in the nodal properties of their orbitals[67]. The assignment of the energy levels of the ML_n groups to the π-MO of polyenes and annulenes has been published[145].

It is clear from this rule that the probability of observing bipyramidal organic molecules or ions is small. Each CH^+ group contributes its 4 electrons. Consequently the central ring must add not more than two π-electrons, i.e. the system must have a high positive charge: +3 for (LXX) and +4 for (LXXI). Such a high electron deficit is impossible simply for electrostatic reasons[137].

On the other hand all the carbaboranes (LXXII)–(LXXV) as well as the bipyramidal (*closo*)dianions of the boranes $B_nH_n^{2-}$ (n = 5–7)[1,138] satisfy the 10*e* rule. The bipyramidal D_{4h} structure has been predicted by calculations[139] for the Li_6 cluster.

VI. THE PRINCIPLE OF THE ISOLOBAL ANALOGY AND THE ELECTRON COUNT RULES FOR POLYHEDRAL ORGANOMETALLIC COMPOUNDS AND CLUSTERS OF TRANSITION METALS

Despite the fact that the atoms of transition elements use not only the valence s- and p-orbitals in the formation of bonds but also the close d-orbitals, the development of ideas concerning the nature of the chemical bond in organometallic compounds and clusters of transition metals has led recently to the discovery of profound analogies between the electronic structures of these compounds and the structurally isotypical compounds of non-transition elements.

1. Isolobal Analogy

An important step towards the discovery of the above analogy was the introduction of the concept of electronically equivalent groups, i.e. groups whose central atoms lack the same number of electrons for the complete filling of the valence electron shell[140,141]. In this sense the Cl atom and the radicals CH_3 and $Mn(CO)_5$, which give rise to the stable dimers Cl_2, C_2H_6, and $Mn_2(CO)_{10}$, are electronically equivalent.

A more exact correspondence between the valence possibilities of groups formed by non-transition and transition elements has been established by the definition by Hoffmann and coworkers[22,142–144] of isolobal (from the English word lobe) groups, i.e. groups for which the number, symmetry properties, forms, and energies of the boundary orbitals are approximately the same. By generating the groups ML_n (n = 2–5) from the ML_6 octahedron as a result of the successive abstraction of two-electron ligands L, Hoffmann and coworkers obtained the MO of the above groups (Fig.12).

The transition metal atom participates in the formation of bonds via nine orbitals: five md-orbitals, one $(m + 1)s$-orbital, and three $(m + 1)p$-orbitals. The three d-orbitals of the axially symmetrical fragment ML_n do not mix with the ligand orbitals and give rise to a low-lying weakly split level, which corresponds closely to the t_{2g} level in octahedral complexes. The interaction of n orbitals of n two-electron ligands with the remaining orbitals of the central atom gives rise to n bonding and n antibonding (not shown in Fig.12) MO of the group ML_n, localised at the M–L bonds. Thus $6-n$ orbitals of the group ML_n remain in the valence band and are filled with $x-2(6-n)$ electrons, where x is the number of valence electrons of the metal.

The group ML_n utilises the above $6-n$ valence orbitals for bonding to other ligands or similar groups. Although these group orbitals involve considerable contributions from the d-orbitals in the metal atoms[22,142–145], their form and symmetry properties are analogous to those of the orbitals of the CH, CH_2, and CH_3 groups examined above (Fig.2). We shall compare the CH and $Co(CO)_3$ groups; the similarity between their boundary a_1- and e-orbitals is readily seen, the cobalt atom in $Co(CO)_3$, like the carbon atom in CH, having three electrons (x = 9 for Co) to fill them. Such

electrons, consumed in the formation of bonds between groups when the latter are combined into skeletal and polyhedral structures, are referred to as skeletal electrons[2-5]. Atomic groups typical for organic structures are compared in the Table with the isolobal and electronically equivalent groups of transition metals.

Isolobal electronically equivalent groups*.

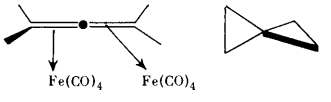
Group	v	$N_{s.e.}$	Group ML_n
CH, N, O+	5	3	$Co(CO)_3$, Ni-(Cp-η^5), $Ir(CO)_3$
CH+, C, BH	4	2	$Fe(CO)_3$, $Os(CO)_3$, Co-(Cp-η^5)
CH^{2+}, C+, BeH	3	1	$Mn(CO)_3$, Fe-(Cp-η^5)
CH^{3+}	2	0	$Cr(CO)_3$, $Fe(CO)_2$, Cr-(C_6H_6-η^6)
CH_2	6	4	$Fe(CO)_4$
CH_3	7	5	$Mn(CO)_5$

* Here ν is the number of valence electrons and $N_{s.e.}$ is the number of skeletal electrons.

Chain, cyclic, skeletal, and cluster structures, obtained by combining isolobal groups, also possess analogous systems of valence orbitals and their structural possibilities are therefore similar. Thus the orbitals of the cyclic clusters $Fe_3(CO)_{12}$ and $Fe_3(CO)_9$ are analogous to the MO of cyclopropane and cyclopropenyl[146] (Fig. 4), while the orbitals of the tetrahedral cluster (I) and their filling with valence electrons are analogous to those of tetrahedrane. Using the idea of the isolobal nature of the η^5-cyclopentadienyl and CH^+ groups, it is easy to show by calculation that the bipyramidal structure (V) meets the requirements of the 10*e* rule [two π-electrons from the five-membered ring and four electrons from each of the BH and Co-(Cp-η^5) groups].

We shall quote some further examples of pyramidal and bipyramidal organometallic structures together with the corresponding non-classical hydrocarbon structures made up of isolobal fragments. Detailed data concerning the structures of the above and other similar organometallic structures are contained in reviews[2-5,125,128,147-149].

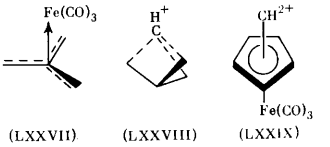
The importance of the concept of isolobal properties is that it constitutes a direct bridge linking the structural ideas of organic chemistry with the involved structural images of the chemistry of transition elements. It makes it possible to discover the analogy between the electronic structures of outwardly completely different classes of organic and organometallic compounds—for example it can be seen that the π-complex (LXXVI) is an organometallic spiropentane:



(LXXVI) (LXIV)

Isolobal analogy ensures a new methodological approach to the search for new non-classical organic structures which can be deduced by replacing the organometallic residues in the structures of π-complexes and clusters by isolobal organic groups (see Table). Thus the structure (XI) of the cation $(CH)_5^+$ might have been predicted on the basis of the structure of the η^4-cyclobutadiene complex of iron tricarbonyl established as early as 1960,[150] while the structure of the dication $(CH)_6^{2+}$ follows from the structure of ferrocene (LV, M = Fe), which became known as early as 1952.[125]

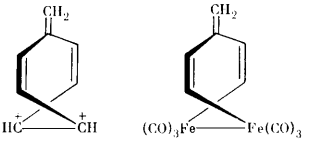
Bearing in mind the stability of the trimethylenemethane complex (XXVII) and the fact that the CH^+ and $Fe(CO)_3$ groups are isolobal, Chandrasekhar et al.[151] suggested the possibility of the existence of the 1-bicyclo[1,1,1]pentyl cation (LXXVIII) and confirmed this hypothesis by a direct MINDO/3 calculation:



(LXXVII) (LXXVIII) (LXXIX)

Although structure (LXXVIII) represents a local minimum on the PES, calculations predict an extremely low energy barrier (1.8 kcal mol^{-1}) in the rearrangement to the 1-methylene-3-cyclobutyl cation. This explains the finding that the intermediate formation of structure (LXXVIII) was not detected in experiments[152] on the distribution of an isotope label in the spiropentyl cation.

At the same time the suggestion that one should seek the bipyramidal dication (LXXIX), put forward by Hogeveen and Kwant[46], is not fruitful, since this structure does not satisfy the 10*e* rule. It must also be emphasised that, in connection with the method of constructing the valence orbitals of the organometallic residues, isolobal analogy should hold most completely for symmetrical compounds where the local symmetry axis of the group coincides with the symmetry axis of the molecule or ion as a whole. Otherwise the correspondence of the non-classical structure generated from a π-complex to a local minimum on the PES must be specially tested. Thus the hypothesis[153] that the dication (LXXX)—an analogue of the bisiron tricarbonyl complex (LXXXI)—can exist was not confirmed by detailed calculations[154], which failed to reveal the corresponding local minimum on the PES of $(CH)_8^{2+}$.



(LXXX) (LXXXI)

2. The Stability of Polyhedral Structures and the Skeletal Electron Count Rules

The stability of the non-classical polyhedral structures of organic molecules and ions examined above can be understood in the context of the general electron count rules developed for skeletal and cluster structures of boranes and heteroboranes and extended, taking into account the ideas of electronically equivalent groups, to the analogous organometallic compounds[2-5,155-157].

These rules are based on the count of skeletal electrons accommodated in the endocyclic orbitals of the skeletal bonds of skeletal and cluster compounds. The number of such electrons is $\nu + x - 2$, where ν is the number of valence electrons of the central atom of a non-transition element occupying one of the vertices and x is the number of one-electron ligands (the unshared electron pair behaves as a phantom ligand). For groups formed by transition metals, the number of skeletal electrons is defined as $\nu + x - 12$. A relation involving electronic equivalence with groups of non-transition elements is then established (see Table). Naturally the difference of 10*e* is in essence the difference

between the requirements for the filling of 8- and 18-electron shells for atoms of non-transition and transition elements.

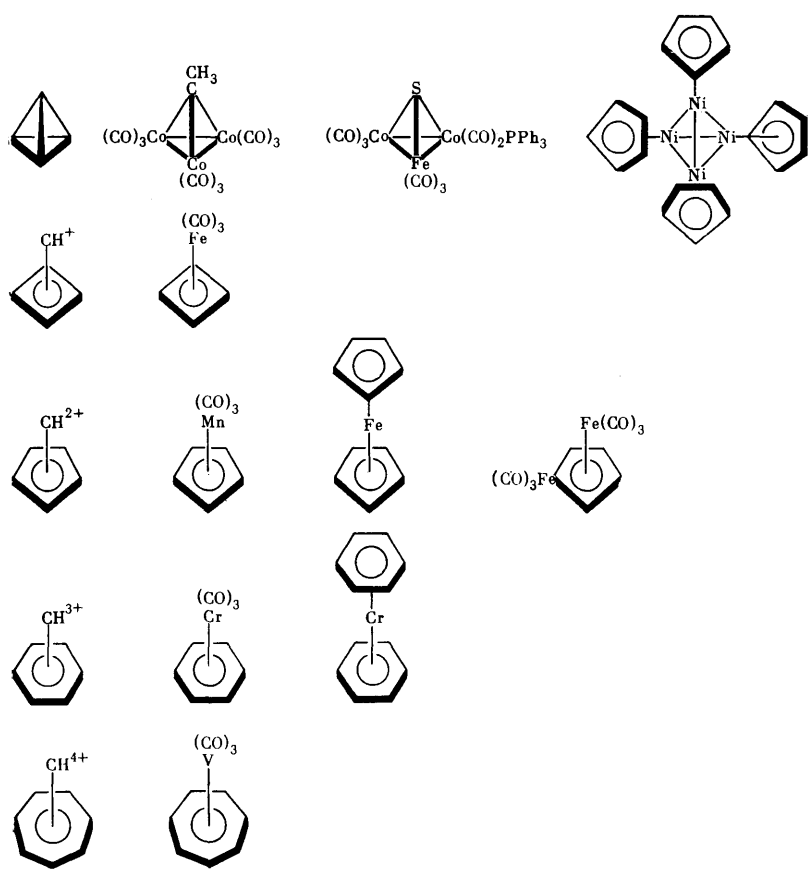
All the polyhedral structures formed by boranes, carbaboranes, heteroboranes, and organometallic compounds, differing by the presence of trigonal faces (deltahedra), can be generated[2-5,40] from the so-called *closo*(closed)-structures of a bipyramidal type for 5–7 vertices, from a trigonal dodecahedron for 8 vertices, etc., *nido*(nest)-structures are obtained from the *closo*-forms by truncating one vertex (for example, pyramids can be obtained from bipyramids). *arachno*(spider-like)-Structures are obtained similarly from *nido*-structures.

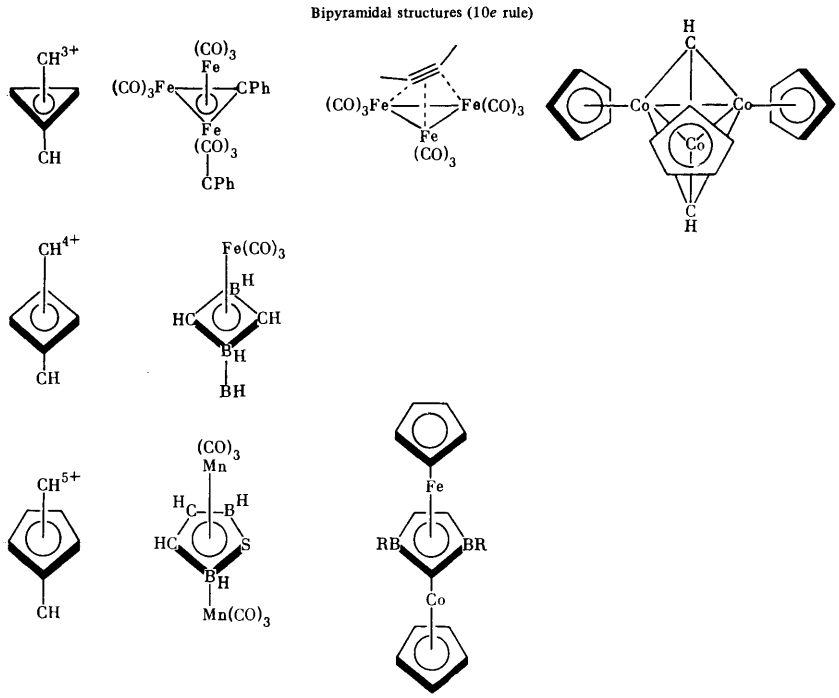
Qualitative analysis[1,2-5,155-158] and direct calculations on *closo*-structures lead to the conclusion that there are $n + 1$ bonding MO for the boranes B_nH_n, in which it is possible to accommodate $2n + 2$ skeletal electrons, i.e. the *closo*-structures of the dianions $B_nH_n^{2-}$ and of the isoelectronic carbaboranes $C_2B_{n-2}H_n$ are stable. The validity of this rule can be readily tested in relation to the bipyramidal compounds (LXXII)–(LXXV). At the same time the hydrocarbons (LXX) and (LXXI) contain respectively 3 and 4 excess electrons, which follows from both the $2n + 2$ and the 10*e* rules.

The $2n + 4$ rule holds for *nido*-structures. The tetraanions $B_nH_n^{4-}$, for example, (XXX), should be stable pyramidal boron hydrides. Finally, for the *arachno*-structure B_nH_n, the number of electrons which can be accommodated in the bonding MO is $2n + 6$, i.e. the hexa-anions $B_nH_n^{6-}$ are stable. For the *arachno*-structures of the hydrocarbons $(CH)_n$, generated by the truncation of the two vertices of bipyramids, i.e. for planar rings, this implies the stability of $(CH)_4^{2-}$, $(CH)_5^-$, $(CH)_6$, and $(CH)_7^+$, which is one of the consequences of the $4n + 2$ Hückel rule.

It is easy to show that the 8*e* and 10*e* rules obtained by reconstruction analysis are equivalent to the $2n + 4$ and $2n + 2$ rules for the skeletal electron count. Indeed in the pyramidal *nido*-structure of type (XXII), which has n vertices, $2(n-1)$ electrons of the $2n + 4$ skeletal electrons form the endocyclic σ-bonds in the basal ring and 2 electrons are used in the exocyclic bond (in the electron pair) of the apical group. The number of electrons binding the above fragments is thus $(2n + 4) - 2(n-1) + 2 = 8$ (the 8*e* rule). For the bipyramidal (*closo*) structure, we obtain analogously $(2n + 2) - 2(n - 2) + 2 + 2 = 10$ (the 10*e* rule).

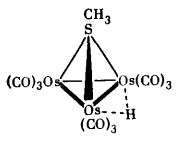
Pyramidal structures (8*e* rule)



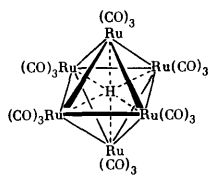


The rules for the counting of skeletal electrons can be readily extended to organometallic compounds, which can be done using the relations in the Table presented above. Other general formulations taking into account not only skeletal but also all valence electrons of skeletal and cluster structures, which are applicable to a wide range of metallic and organometallic structures with between 5 and 15 vertices[159,160] and also to skeletal and cluster electron-excess structures of the chalcogenides[161], have also been proposed.

Bridging groups, for example hydrogen atoms, can play the role of suppliers of skeletal and inner electrons. Thus the neutral *closo*-boranes B_nH_{n+2} correspond to the *closo*-dianions $B_nH_n^{2-}$, while the *nido*-borane B_nH_{n+4} [for example, B_5H_9 (XVI)] corresponds to the *nido*-tetra-anion $B_nH_n^{4-}$. In cluster (III) the carbon atom incorporated in the pyramidal skeleton contributes four additional electrons, with the aid of which the 8*e* requirement is met. We shall present further examples of the pyramidal [compound (LXXXII)][162] and bipyramidal [compound (LXXXIII)][163] clusters in which the bridging and endocyclic hydrogen atoms build up the inner electron shells to 8*e* and 10*e*:



(LXXXII)



(LXXXIII) $[H \cdot Ru_6(CO)_{18}]^-$

Using the technique of reconstruction analysis, it is possible to show that the bridging groups do not in fact alter the fundamental bonding pattern in polyhedral structures (Figs. 5 and 11). Analysis of the structures of the MO of a series of organometallic compounds with bridging hydrogen atoms has been described[164-166].

The importance of the electron count rules examined above is that they bring into direct correspondence the number of bonding MO and the type of polyhedral structure regardless of the nature of its constituent apical groups. These rules are topological in nature and clearly demonstrate the fact that inorganic and organic chemistry have common structural principles. This is confirmed also by the possibility of extending the relation

$$closo \underset{-2e}{\overset{+2e}{\rightleftharpoons}} nido \underset{-2e}{\overset{+2e}{\rightleftharpoons}} arachno \qquad (8)$$

which is familiar for boranes and carbaboranes, to polyhedral organic structures in the form

$$(n-2)\text{-gonal bipyramid } (10e) \underset{-2e}{\overset{+2e}{\rightleftharpoons}} (n-1)\text{-gonal pyramid}$$
$$(8e) \underset{-2e}{\overset{+2e}{\rightleftharpoons}} n\text{-gonal ring } (6e) \qquad (9)$$

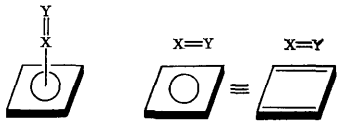
The reaction whereby the dication (XIIb) is obtained from Dewar hexamethylbenzene[46] as well as the reaction (XXIX) $\rightleftharpoons$ (XXV, Y = S^{2+}) are examples where Eqn. (9) holds.

VII. [*n*]PRISMANES AND OTHER POLYHEDRA

Apart from the combinations of structural units of polyhedra described above, there is also a possibility of edge–edge, edge–face, and face–face fusion.

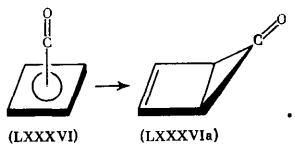
The interactions of π-bonds and conjugated chains, which correspond to the type of edge–edge interaction, have been analysed[38,39]. Two topologically different perpendicular [structure (LXXXIV)] and parallel [structure (LXXXV)] orientations of the face and edge, ensuring the interaction of the entire system of ring orbitals with the orbitals of the π-bond, are illustrated below in relation to a four-membered

ring:



(LXXXIV) (LXXXV) (LXXXVa)

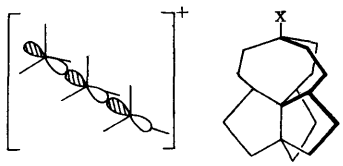
The valence orbitals of the groups X = Y (C≡O, N≡CH, N=O, S=O, O=O)[34,37] are similar in form to the CH group orbitals (Fig. 2), the antibonding π_x^*- and π_y^*-orbitals of the group XY corresponding to the pair of p_x- and p_y-orbitals. Since the *e*-level of these orbitals lies high above the *e*-level of the π-orbitals of the ring, this main type of interaction stabilising the pyramidal structures (LXXXIV) is weakened. Therefore, even in the most favourable case with XY=CO,[167] the above orbital interactions are sufficiently strong for the overall stabilisation of the (LXXXIV) system. Thus non-empirical (STO-3G)[168] and MINDO[169] calculations have shown that a local minimum in the PES of C_4H_4CO does not correspond to the C_{4v} structure (LXXXVI)[44] and the latter relaxes to the structure of bicyclo[2,1,0]pentenone (LXXXVIa):



(LXXXVI) (LXXXVIa)

The hypothesis[65,171,172] of the intermediate structure (LXXXIV, XY=SO) in the topomerisation reaction of Dewar thiophen oxide, analogous to the rearrangement (XXIa) ⇌ (XXIb), has not been confirmed by calculations[170].

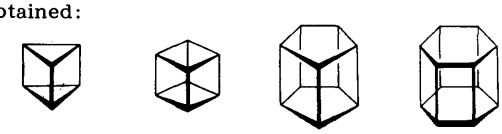
A more favourable orientation of the orbitals of the [*n*]-annulene ring and of the π-bond is attained in the configuration (LXXXV) predicted by calculations[168] for complexes of cyclobutadiene with C≡O, HC≡N, and CO_2. Discussion of the structures of these complexes has attracted considerable attention in connection with their intermediate formation in the photolysis and thermolysis of the precursors of cyclobutadiene derivatives[173–175]. The main type of orbital interactions in this configuration, namely $\pi_\sigma-\pi_\sigma$ interactions, has been considered recently with the aid of six different semi-empirical and non-empirical computational methods[176] in relation to the simple but structurally important model of the non-classical σ-allyl cation $(CH_3)_3^+$ (LXXXVII), in which the three methyl groups are bound together by the $p_\sigma-p_\sigma$ interactions of three *p*-orbitals:



(LXXXVII) (LXXXVIIa)

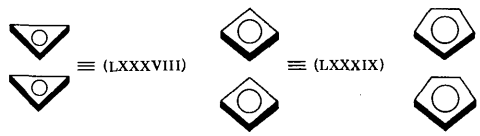
Since this type of interaction results in the formation of bonding, non-bonding, and antibonding MO, this configuration is stabilised in the two-electron case (cation). This suggests that fairly stable cations—analogues of the σ-allyl cation (LXXXVII)—can be generated from a suitable precursor, for example, propellane (LXXXVIIa).

The considerable role of the $\pi_\sigma-\pi_\sigma$ interactions between the orbitals of [*n*]annulene rings in the stabilisation of the polyhedral structure can be traced[177] in relation to [*n*]prismanes. The $(CH)_{2n}$ clusters with D_{nh} symmetry belong to this series. The first member of the series, namely [3]prismane (LXXXVIII) (triprismane according to Schultz's nomenclature[180] for compounds of this type) and tetraprismane (LXXXIX), also known as cubane, have been synthesised and studied in detail theoretically[14,37,100,178,179]. The higher representatives of the series of [*n*]prismanes, namely pentaprismane (XC), hexaprismane (XCI), etc., have not so far been obtained:



(LXXXVIII) (LXXXIX) (XC) (XCI)

The structures and the MO of prismanes can be formed by the parallel superposition of two identical [*n*]annulene rings (face–face interactions):



≡ (LXXXVIII) ≡ (LXXXIX) ≡ (XC)

Two main types of interactions of the fragment orbitals can then be distinguished: π-overlap of a σ-MO of the Walsh type ($\sigma_\pi-\sigma_\pi$ interaction) and the σ-overlap of the π-MO ($\pi_\sigma-\pi_\sigma$ interaction). The above orbitals are illustrated in Fig. 4 in relation to [3]annulene. The interaction between the completely filled σ-MO are of the repulsive, destabilising type. However, the magnitude of this effect is comparatively small, since it is approximately proportional to the square of the overlap integral [see Eqns. (4) and (5)]. The $p_\pi-p_\pi$ overlap integral does not exceed 0.15 for equilibrium distances, while the $p_\sigma-p_\sigma$ overlap integral reaches 0.35. Because of this, the interaction (splitting) of the π-MO is significantly stronger. The main cause of stabilisation by such interaction is that the in-phase overlap of the identical antibonding π-MO of [*n*]annulenes leads to such a pronounced splitting of their levels that the lowest level becomes the bonding MO of [*n*]prismane (Fig. 13).

This result is obtained only under the conditions of a close parallel approach of the [*n*]annulene rings. For distances of the order of magnitude of the van der Waals contacts, the $p_\sigma-p_\sigma$ overlap integral is small and the splitting of the π-levels is insufficient to overcome the repulsive interactions (Fig. 13). This has been confirmed by direct calculations of the interaction energy of two benzene molecules[168,181] and also by structural data for benzene dimers obtained by the method of molecular beams[182], which show that the perpendicular orientation of the planes of the rings in the dimer is preferable.

The unfavourable nature of the [*n*]prismane structures for clusters of other elements can be understood from the correlation MO diagram in Fig. 13. The D_{2d} structure of the *closo*-dianion $(BH)_8^{2-}$ is more favourable by almost 400 kcal mol^{-1} than the cubic structure of the O_h type (LXXXIX)[183], since $(BH)_8^{2-}$ has only two electrons to fill all the bonding MO of the O_h structure (Fig. 13). On the other hand, the polychalcogenides S_8, S_8^{2+}, S_4N_4, and Se_{10}^{2+} [161] would have several antibonding MO populated by electrons in the [*n*]-prismane form. At the same time cluster (VI), which is isoelectronic with cubane (LXXXIX), has a structure similar to the latter.

The conditions for the stabilisation of the structure as a consequence of the formation of bonding MO, obtained by the in-phase combination of the antibonding MO of the fragments, which has been considered in relation to [*n*]prismanes, is fairly general for skeletal organic compounds. It is readily

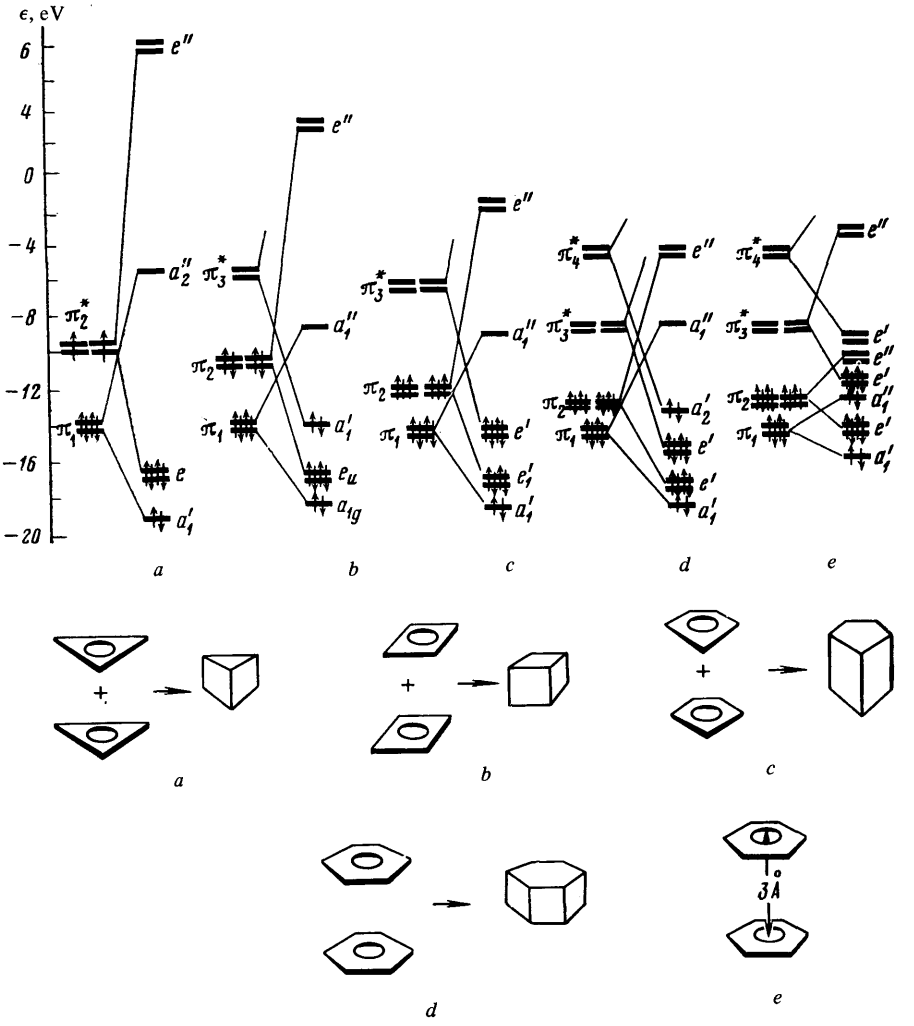
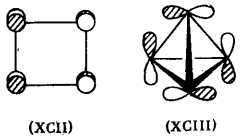


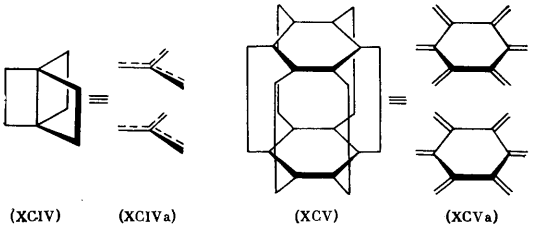
Figure 13. Schematic illustration of the formation of the MO of [*n*]prismanes as a result of the $\pi_\sigma-\pi_\sigma$ overlap of the π-MO of the [*n*]annulene fragments[177]. The energy levels of the annulenes and the overlap integrals of the π-MO for the equilibrium distances in [*n*]prismane have been obtained by calculations using the extended Hückel method (the $p_\sigma-p_\sigma$ overlap integral was assumed to be 0.3). The splitting of the levels following the approach of two benzene molecules to a distance exceeding the equilibrium distance in [6]prismane and equal to the sum of the van der Waals radii of the carbon atoms (the $p_\sigma-p_\sigma$ overlap integral is 0.1), for which the dimer is unstable, is shown on the right-hand side of the Figure. The correlation diagrams (*a*)–(*e*) correspond to structures (*a*)–(*e*).

seen that components of the highest occupied MO of cyclobutadiene (XCII) and tetrahedrane (XCIII) are made up of antibonding π*-MO of acetylenic fragments (cf. Fig.3):



(XCII) (XCIII)

The structures of the highest occupied MO of [2.2.2]propellane (XCIV)[44] and of the molecule of superphane (XCV) synthesised recently[184] also correspond to the case considered.



(XCIV) (XCIVa) (XCV) (XCVa)

On the other hand, the analogous parallel superposition of [5]- and [3]-annulenes does not lead, following their mutual approach in different relative orientations, to the appearance

of local minima of the biradical type on the PES of $(CH)_8$.[177] Analysis of the orbital interactions of the three-membered rings of $Fe_3(CO)_9$ and [5]annulene also leads to the conclusion that there is no stabilising effect. The structural consequences of the orbital interactions of the polyene chains and rings with the edges, faces, and individual vertices occupied by isolobal CH^{n+} groups and organometallic fragments have been examined in a number of studies[22,23,146].

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The approach to the study of the nature of the stabilisation of molecules and ions with a strained or non-classical structure which has been considered here is applicable to the entire branched series of skeletal and polyhedral structures. The possibility of formulating electron count rules for inner, skeletal, or all valence electrons, which are valid for specific structural types regardless of whether the structure belongs to the series of organic, organometallic, or inorganic compounds, emphasises both the fact that the principles of electronic structure are common to these compounds and the decisive role of topological factors in their orbital organisation.

Like any broad generalisation, these rules have many exceptions. In the present review we did not concentrate attention on these, since the causes of the deviations from the predictions based on the electron count rules can be understood and foreseen on the basis of the same research techniques which have led to the formulation of the rules and also on the basis of more rigorous schemes for the fragmentation of structures.

The deviations from the rules formulated above are most frequently seen in the effect of substituents. Such are the sharp deviations from the classical structures of hydrocarbons where hydrogen atoms are replaced by lithium atoms or BH groups[98,185-187] and conversely the stabilisation of classical structures following the replacement of hydrogen atoms in carbaboranes by halogen atoms[188]. Direct allowance for the orbitals of the substituents within the framework of the scheme of reconstruction analysis explains the above effects.

The orbital approach to the analysis of complex structures has been recently extended as far as the field of the crystal chemistry of organic and inorganic compounds[189]. It has been shown that $\pi_\sigma - \pi_\sigma$ interactions of the orbitals of the A_6 and A_3X_3 hexagonal cells actually determine the structures of the crystal lattices of graphite, sphalerite, wurtzite, etc.

This approach has become a powerful instrument for the molecular design of new unusual organic structures and their organometallic analogues.

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Molecules with a High Electron Affinity

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Experimental values of the electron affinity of inorganic compounds reported between 1975 and 1980 are systematically examined. The following methods of measuring electron affinity are briefly reviewed: photo-extraction and photoelectron spectroscopy, electron impact, ion-molecule reactions, ionisation by alkali metal atoms, ion-molecule equilibria, and methods based on measuring the frequency for intramolecular charge transfer in the absorption spectra of complexes and on calculations using a thermochemical cycle. Classes of compounds having an electron affinity greater than that of halogen atoms are identified by analysing published data. 166 references.

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I. INTRODUCTION

In the early 1970's very few substances with an electron affinity higher than that of the halogen atoms were known, and it was generally assumed that positive values of the electron affinity must lie in the range 0–4 eV. However, experimental methods of measuring electron affinity were being actively developed[1,2], and the first reports of compounds with very much higher electron affinities were beginning to appear[3]. These compounds are the strongest known oxidising agents, they readily form stable negative ions, and they lower the concentration of electrons in flames and plasmas.

In this paper we shall review experimental methods of measuring electron affinities, their validity when applied to substances with a high electron affinity, and the results obtained in the period 1975–1980. References to earlier work can be found in recent monographs[1,2]. Franklin and Harland's review[4] gives an account of experimental methods of studying negative ions and of the results obtained up to 1974, and it lists earlier reviews on negative ions (published since 1950). The most reliable information on the electron affinity of inorganic and of organic molecules published up to 1975 is summarised by Rosenstock and coworkers[5]. Between 1978 and 1980 four more reviews were published[6–9]; these contain more recent results and they partly overlap the present discussion.

Standard methods of determining electron affinities include the threshold methods, in which the affinities are calculated from the minimum energy of an impinging particle which will lead to the formation or breakdown of a negative ion. Among these methods are the photo-extraction and the electron impact method, and also methods based on the formation of negative ions by ion–molecule reactions or by collisions between neutral particles. Another large group of methods can be described as "equilibrium" methods, because the measurement consists in determining the temperature dependence (or the absolute value) of the equilibrium constant of a reaction involving the negative ion. This group includes the magnetron method and the surface ionisation method, and also the study of equilibria in gases, flames, and plasmas, and the classical effusion method, which was only very recently modified to deal with the special problems met in the determination of electron affinities.

Theoretical calculations of the electron affinity lie outside the scope of this review. The relevant methods are briefly outlined in Refs.1,2, and 7. Recent theoretical calculations of the electron affinity of hexafluorides are reported in Refs.10–12. Some of the more obscure methods which have been used to measure electron affinities are mentioned in Refs.1 and 2. In the latter part of this review we shall discuss two semiquantitative methods for estimating the electron affinity of complex molecules such as hexafluorides. The first is based on a calculation by the Born–Haber thermochemical cycle (see, for example, Ref.1), which includes the heats of reactions between charged particles and neutral particles. This method relies on theoretical calculations of the crystal lattice energy. The second method is based on a study of the absorption spectra of complex molecules, coupled with an experimental determination of the frequency of the transition corresponding to the intramolecular charge transfer process. Theoretically[13] this frequency is related to the ionisation potential of the electron donor and the electron affinity of the acceptor. The electron affinity of the acceptor molecule can therefore be estimated.

II. PHOTO-EXTRACTION AND NEGATIVE ION PHOTOELECTRON SPECTROSCOPY

For a more detailed discussion of the topics examined in this Section the reader is referred to recent monographs[1,2] and papers[14,15]. Both methods depend on a calculation of the energy balance in the photo-extraction of an electron from a negative ion:

$$AB^- + h\nu = AB + e \ .$$

Two distinct approaches have been used. In the first the frequency of the radiation is varied, and the threshold energy for the photo-extraction of the electron is found experimentally; in the second the radiation frequency is fixed and the kinetic energy spectrum of the emitted electrons is recorded. Since the kinetic energy spectrum characterises the energy levels of the negative ion, the term "negative ion photoelectron spectroscopy" has been proposed for

this variant. In the case of atomic anions the interpretation of the results is unambigous, and the experimental values of the frequency and energy of the emitted electrons can be used to calculate the electron affinity of the atom with high precision (Table 1): some workers[16] quote an uncertainty of ±0.0003 eV. For molecular anions the calculated value corresponds to a vertical transition, and in general this is not the same as the electron affinity of the molecule (defined as the energy difference between the ground states of the molecule and the ion). The difference between a vertical and an adiabatic transition can be large, especially in the case of molecules with a large electron affinity.

Table 1. Electron affinities determined by photo-extraction (PE) and photo-electron spectroscopy (PES) methods.

Molecule	E_i, eV	Method	Reference
AsH	1.0±0.1	PE	[20]
As_2	0	PE	[21]
BeH	0.7±0.1	PE	[20]
CD_2O	1.552±0.022	PES	[22]
CD_2S	1.858±0.006	PE	[23]
CH	1.238±0.008	PES	[24]
CH_2	0.21±0.03	PES	[25]
CH_3	0.08±0.03	PES	[26]
CH_3	1.882±0.024	PES	[22]
CH_3O	1.570±0.022	PES	[22]
CH_3O	1.59±0.04	PE	[27]
CH_3	1.86±0.04	PE	[23]
CO_3	2.69±0.14	PE	[28]
CO_3	2.9±0.3	PE	[19]
CO_3	3.26±0.17	PE	[29]
C_2	3.391±0.017	PE	[30]
C_2H	2.97±0.10	PE	[18]
CaH	0.93±0.05	PE	[20]
FeCO	1.26±0.02	PES	[31]
$Fe(CO)_2$	1.22±0.02	PES	[31]
$Fe(CO)_3$	1.8±0.2	PES	[31]
$Fe(CO)_4$	2.4±0.3	PES	[31]
FeO	1.492±0.020	PES	[17]
LiCl	0.61±0.02	PES	[32]
MgH	1.05±0.06	PE	[20]
NH	0.381±0.014	PES	[33]
NO_2	2.5	PE	[34]
O_3	2.102±0.025	PE	[35]
PH	1.028±0.010	PES	[36]
PH	1.00±0.06	PE	[20]
PH_2	1.271±0.010	PES	[36]
PO	1.092±0.010	PES	[36]
P_2	0.65	PE	[21]
S_2	2.00±0.15	PE	[21]
SiH	1.277±0.009	PES	[37]
SiH_2	1.124±0.020	PES	[37]
ZnH	0.95	PE	[20]

Experimental studies of the photo-extraction of electrons from negative ions are fairly complicated, and include a number of steps (not least, the generation of a strong beam of negative ions). The early work was carried out by the crossed beam method[1], in which the source of ions is a glow discharge and the ions emerge from a slit in the anode with an energy of ~ 300–500 eV and an energy spectrum 25–50 eV wide. The ion beam is accelerated, collimated, and after passing through the mass separator it enters the photon interaction region. The light source was either an argon ion laser working at 4880 and 5145 Å (2.5 and 2.4 eV) or a dye laser with a continuously swept frequency in the energy range 1.75–2.4 eV. The experiment consisted in recording the kinetic energy spectrum of the emitted electrons and measuring the threshold value of the photon energy (i.e. the minimum photon energy giving rise to photo-extraction).

Thus, Engelking and Lineberger[17] produced a strong beam of FeO^- and O^- ions in a low-pressure electric discharge, struck by burning iron pentacarbonyl in oxygen or nitrous oxide. The ions were accelerated to 680 eV and mass-separated in a Wien filter. The ion beam was crossed with a photon beam of 2.5 eV energy (4880 Å). The emitted electrons were energy-analysed, using an electrostatic monochromator with a resolution of 0.06 eV. The electron energy scale was calibrated by using the O^- ions present in the same discharge. As a result the electron affinity of the FeO molecule was found[17] to be $E(FeO) = 1.492 \pm 0.020$ eV.

In another type of apparatus ion–cyclotron resonance is used. This method does not require an accelerating voltage for mass separation, and the ions move from the source region to the analyser with near-thermal velocities. The time of residence of the ion in the apparatus is of the order of seconds: this is the most attractive feature of the "ion–cyclotron resonance + photo-extraction" method. The use of ion–molecule reactions to generate negative ions becomes possible. The primary negative ions are formed by collisions between neutral molecules and electrons (emitted by a thermionic cathode), and these ions take part in ion–molecule reactions during their subsequent slow drift within the source. The list of negative ions which can be studied has been greatly increased by the advent of this method. Janousek and coworkers[18] determined the electron affinity of the C_2H radical in an apparatus which included a V-5900 ion–cyclotron resonance spectrometer. The pressure in the drift region was 2×10^{-7} mmHg, the life time of the ions was ~ 0.5 s. The C_2H^- anions were obtained by the ion–molecule reaction $C_2H_2 + F^- \rightarrow C_2H^- + HF$. The source of F^- was the dissociative ionisation of nitrogen trifluoride by electron impact ($NF_3 + e \rightarrow NF_2 + F^-$). The electron affinity value obtained in these experiments was $E(C_2H) = 2.94 \pm 0.10$ eV.

A study of negative molecular ions relevant to the chemistry of the *D* layer in the ionosphere was carried out in the molecular physics laboratory of the Stanford Research Institute[19]. This work was aimed mainly at determining the photo-dissociation and photo-extraction cross-sections of ions such as $O_2^-.O_2$, $O_2^-.H_2O$, $O_3^-.H_2O$, CO_3^-, CO_4^-, HCO_3^-, $HCO_3^-.H_2O$, $NO.O_2^-$, $NO.O_2^-.H_2O$, and $NO_2^-.H_2O$. The measurements of cross-section could (in some cases) be interpreted in terms of the threshold values of the photo-extraction energy, and in these cases the electron affinity was calculated. The apparatus used in this work included a mass spectrometer with a drift tube. The negative ions were produced by collision with electrons emitted from a thorium–iridium cathode, and by the subsequent ion–molecule reactions in the drift tube. The ion source and the drift tube were filled with the gas (or gas mixture) at 0.05–1.0 mmHg pressure. The ions drifted (under the influence of a weak electric field) with an average velocity about an order of magnitude lower than the thermal velocity. During their drift time the ions undergo enough collisions with neutral particles to come to thermal equilibrium with the medium, and the excess energy acquired by the ions during their formation relaxes. This is one of the main advantages of the method, since it eliminates errors arising from the presence of ions in excited states and possessing an excitation energy much greater than the thermal energy. Approximately 2 mm beyond the exit slit of the drift tube the ions cross a modulated photon beam generated either by a dye laser with a continuous spectrum in the region of 4250–4600 Å or by an argon or krypton ion laser with a discrete set of lines at 4067–5309 Å. Beyond the exit slit the ions enter the high-vacuum region, which includes a quadrupole mass spectrometer. After mass separation the ions are recorded in a two-channel counter in the presence (I) and in the absence (I_0) of laser radiation. The percentage breakdown of the ions is small, and the I/I_0 ratio is close to unity. Therefore the signal needs to be integrated over a fairly long time: from minutes to hours, depending on the photo-extraction cross-section.

The method has been used also to determine the electron affinity of carbon trioxide[19]: the result was $E(CO_3) = 2.9 \pm 0.3$ eV. Electron affinity values obtained by the photo-extraction and photo-electron spectroscopy method and published between 1975 and 1980 are listed in Table 1.

III. ELECTRON IMPACT

Negative ions can be formed in several ways during electron impact. However, direct electron capture is not very effective because of the need to transfer the affinity energy to a third body, or to dissipate this energy among the internal degrees of freedom of the molecule. Processes leading to the formation of ion pairs have been successful, but only for atoms[1]. Therefore only the dissociative electron capture process has been widely used to measure electron affinities. The most recent review of dissociative electron attachment processes is given in Ref.38, and earlier work is discussed in Refs.4 and 39.

Table 2. Electron affinities determined by the electron impact method.

Molecule	E, eV	Reference	Molecule	E, eV	Reference
AsBr	1.3	[40]	$NaBO_2$	1.43 ± 0.22	[47]
$AsBr_2$	3.5	[40]	$NbCl_4$	1.4	[50]
AsCl	1.3	[40]	PCl_3	0.95	[51]
$AsCl_2$	2.2	[40]	PF_3	3.7	[52]
AsF	1.3	[40]	$SiBr_2$	1.7; 1.9	[46]
AsF_2	0.8—0.9	[40]	$SiCl_2$	0.64; 0.90	[46]
C_2F_3	$\geqslant 1.6$	[41]	$SnBr_2$	1.33	[53]
C_3F_5	~ 3.0	[41]	$SnBr_3$	3.31	[53]
ClF	2.37 ± 0.21	[42]	$SnBr_3$	3.08	[51]
ClF_2	$\geqslant 0.9 \pm 0.2$	[42]	$SnCl_2$	1.04	[53]
ClF_2	$\geqslant 3.23 \pm 0.19$	[43]	$SnCl_3$	2.53	[53]
ClF_3	$\geqslant 2.40 \pm 0.10$	[43]	SnF_3	$\geqslant 1.2$	[53]
ClO	2.35 ± 0.12	[44]	SnI_2	1.74	[53]
ClOF	2.00 ± 0.19	[44]	SnI_3	3.21	[53]
ClO_2	1.80 ± 0.16	[44]	$TaCl_4$	>1.4	[50]
$(CrO_3)_2$	1.6	[45]	$TiBr_3$	0.76	[51]
$(CrO_3)_3$	1.8	[46]	$TiCl_3$	0.61	[51]
$GeBr_2$	1.6; 1.8	[46]	$VOCl_3$	$\geqslant 3.6$	[54]
$GeCl_2$	2.56	[46]	VOF_3	3.1 ± 0.3	[54]
$GeCl_3$	1.83	[46]	WF_4	2.6	[55]
KBO_2	1.17 ± 0.22	[47]	WF_4	$\geqslant 1.0$	[56]
NF_2	0.4 ± 0.2	[48]	WF_5	1.25 ± 0.2	[55]
NF_2	$\geqslant 0.7 \pm 0.2$	[49]	WF_5	$\geqslant 0.4$	[56]
			WOF_3	$\geqslant 0.3$	[56]

The dissociative electron capture process is described by the reaction $AB + e \rightarrow A + B^-$. The lower limit of the electron affinity of the molecule, $E(B)$, can be found from the threshold value of the electron energy, E_e, if the bond breaking energy $D(A-B)$ is known:

$$E(B) \geqslant D(A—B) - E_e + T ,$$

where T is the combined kinetic energy of the A and B residues. The inequality sign allows for the possible generation of the dissociation products in an excited state. Electron affinity values obtained in 1975—1980 by the electron impact method are listed in Table 2.

IV. ION—MOLECULE REACTIONS

When the collision between a negative ion and a neutral particle results in an endothermic reaction it is possible, in principle, to determine the enthalpy of formation of the negative ion and the electron affinity. In the simplest case, when the reaction consists simply in the exchange of an electron, the threshold value of the energy of the mutually repelling particles which leads to charge transfer gives the difference in electron affinity between the molecules taking part in the reaction. The electron affinities of halogen molecules[57] and oxygen compounds[58] have been obtained in this way:

Molecule	F_2	Cl_2	Br_2	I_2	O_2	O_3	NO	NO_2	NO_3
E, eV	3.08	2.38	2.51	2.58	0.48	1.96	0.09	2.04	$\geqslant 2.49$

The measurements consisted in determining the threshold energy of processes such as $F^- + F_2 \rightarrow F_2^- + F$, which corresponds to the difference in electron affinity between the atom and the molecule.

Charge transfer processes can be accompanied by chemical reactions leading to the formation of new ions and molecules. The threshold energy of the colliding particles gives the enthalpy of the reaction, and the possibility of calculating the electron affinity arises when the enthalpies of formation of all the other participants in the reaction are accurately known. A good illustration of this method is provided by an experimental determination[49] of the threshold energy (found to be 0.64 eV) for reactions of the type of

$$I^- + HNO_3 \rightarrow NO_3^- + HI .$$

This quantity is the enthalpy of the reaction, and since the enthalpies of formation of I^-, HNO_3, and HI are known, the enthalpy of formation of the NO_3^- ion can be calculated: $\Delta H_f^\circ(NO_3^-) = -3.04 \pm 0.09$ eV. In order to determine the electron affinity we must know $\Delta H_f^\circ(NO_3)$. Using the published value of this parameter the authors[49] obtained $E(NO_3) = 3.77 \pm 0.25$ eV.

Another example of the prospects of ion—molecule reactions is provided by a study[60] of the dissociation of negative ions by collisions with inert gas atoms. In this work a more complicated technique was used to produce the beam of negative ions. Whereas in the work described above[49] the range of negative ions was very limited, and only processes giving rise to a single type of negative ion could be used, in Ref.60 a mass separation of the negative ions was carried out as the first stage in the process. As a result, any method of ionisation could be used, including methods which yield a large number of different negative ions. After mass separation the ion beam passed through a 90° electrostatic analyser which selected the ions having a prescribed energy in the range 0.3—170 eV with an energy scatter of 0.2—0.3 eV. These ions have a known kinetic energy when they reach the collision chamber, where they undergo endothermic ion—molecule reactions to form new ions which are detected in a second mass spectrometer. The experiments consist in determining the minimum energy of the colliding ions for which reaction products are formed. The technique has been used[61] to study the dissociation of negative ions on the gases A (Xe, Kr, Ar, Ne, He, and N_2). The average value of the threshold energy for the reaction $N_2O^- + A \rightarrow N_2 + O^- + A$ was 0.43 eV, which can be combined with published data on the bond energy $D(N_2—O)$ and on $E(O)$ to give $E(N_2O) = 0.22$ eV.

Ion—cyclotron resonance apparatus is widely used in studies of ion—molecule reactions, usually for exothermic reactions which take place at thermal energies between the colliding particles. Hence the pair of particles on which the electron affinity is measured must be chosen so that the charge transfer reaction can proceed in one case but not in the other. This allows both the upper and the lower limit of the electron affinity of the given molecule to be determined. The electron affinity of tungsten hexafluoride has been determined in this way[62]. Charge transfer was shown to occur with fluorine but not with chlorine, and hence the value $E(WF_6) = 3.5 \pm 0.1$ eV was obtained.

In an earlier study[63] an attempt was made to measure the threshold energies of ion–molecule reactions directly. A beam of negative UF_6^- ions was produced by surface ionisation of uranium hexafluoride on a rhenium filament at 800–900 K, i.e. at a temperature giving a negligibly small electron emission current. The energy of the UF_6^- anions was varied between 0 and 40 eV, and the threshold values of the energy for the following reactions were identified[63]:

$$UF_6^- + UF_6 \rightarrow UF_7^- + UF_5$$
$$UF_6^- + BF_3 \rightarrow UF_5 + BF_4^- ,$$

leading to the affinities of uranium hexafluoride for electrons and for the fluoride ion shown in Table 3.

Table 3. Electron activities obtained from the threshold energies of ion–molecule reactions.

Molecule	E, eV	Reference	Molecule	E, eV	Reference
BrO	$\geqslant 1.5 \pm 0.2$	[66]	NaCl	0.77	[71]
Cl	3.4	[67]	NaF	0.42	[71]
CO	1.37	[67]	OCN	3.6 ± 0.2	[64]
CO_3	$\geqslant 2.80$	[68]	O_3	$\geqslant 1.8234$	[68]
ClO	$\geqslant 1.6 \pm 0.2$	[66]	O_3	$\geqslant 2.26 + 0$ [04	[73]
IN	1.3	[69]		-0.06	
IO	2.6	[67]	SF_2	3.4 ± 0.2	[74]
IO	2.3	[70]	SF_5	>3.45	[74]
IO	$\geqslant 2.1 \pm 0.3$	[66]	SO	1.2	[70]
KBr	0.61	[71]	SO_2	1.05	[70]
KCl	0.63	[71]	SO_2Cl	<3.17	[75]
KF	0.23	[71]	SO_2F	<2.34	[75]
NO	0.8 ± 0.2	[69]	UF_5	2.4	[63]
NO_2	2.1	[69]	UF_6	4.9 ± 0.5	[63]
NO_3	3.77 ± 0.25	[59]	UF_6	$\geqslant 3.61$	[76]
N_2O	0.22 ± 0.11	[61]	UF_6	>5.0	[77]
NaBr	0.94	[71]	UF_7	$\leqslant 5.5$	[63]
			WF_6	3.51 ± 0.1	[62]

Another possible way of determining thermochemical quantities by using ion–cyclotron resonance apparatus involves measuring the equilibrium constants of ion–molecule reactions. Thus, in an experimental study[64] of the reaction

$$HCO_3^- + HNCO \rightleftarrows OCN^- + HCO_2H$$

the rate constants of the forward (k_f) and of the reverse (k_r) reaction were determined, and the equilibrium constant $K = k_f/k_r$ was calculated. The equilibrium constants obtained in this way agreed exactly with the values directly determined by measuring the concentration ratios of the ions and molecules under conditions giving long residence times of the ions in the reaction zone. By combining the result with published data on the enthalpy of formation of the reactants and products the authors[64] obtained $E(OCN) = 3.62 \pm 0.2$ eV for the electron affinity of the OCN radical.

A new method of calculating electron affinities from studies of electron extraction by glancing-angle impact has been proposed[65]. Negative ions (B^-) having a high kinetic energy (~ 6000 eV) can be converted into B^+ ions by glancing-angle collisions with neutral molecules:

$$B^- + N \rightarrow B^+ + N + 2e \cdot$$

If both B^- and B^+ are in their electronic ground state the difference in their kinetic energies is equal to the sum of the ionisation potential $I(B)$ and the electron affinity $E(B)$ of the B molecule. If $I(B)$ is known, we can calculate the electron affinity by measuring the difference between the kinetic energies of the B^- and the B^+ ion. For example, $E(CN) = 3.3$ and $E(S_2) = 2.15 \pm 0.5$ eV have been determined in this way[65], in good agreement with published data. Electron affinities obtained in 1975–1980 from studies of ion–molecule reactions are given in Table 3.

V. IONISATION BY COLLISION OF NEUTRAL PARTICLES

Collisions between neutral particles can lead to the formation of ion pairs, thus allowing electron affinities to be determined from the threshold value of the energy of the colliding particles. Under these conditions the threshold energy directly gives the difference between the ionisation potential and the electron affinity of the particles. The formation of ion pairs by collisions between neutral particles is discussed in Ref.78.

Table 4. Electron affinities determined by ionisation with alkali metal atoms.

Molecule	E, eV	Reference	Molecule	E, eV	Reference
AuF_6	10.0 ± 0.5*	[82]	NO_3	3.7 ± 0.2	[91]
BBr_3	0.8 ± 0.2	[83]	O_2	0.44	[95]
$BClBr_2$	0.9 ± 0.2	[83]	O_3	2.14 ± 0.15	[96]
BCl_2Br	0.7 ± 0.2	[83]	$PBrCl_2$	1.5	[97]
BCl_3	0.3 ± 0.2	[83]	PBr_2Cl	1.6	[97]
BF_3	0.0 ± 0.2	[83]	PBr_3	1.6	[97]
Br_2	2.6 ± 0.2	[84]	PCl_3	0.8	[97]
CCl_2	1.8 ± 0.3	[85]	$POCl_2$	3.8	[97]
CCl_3	1.3 ± 0.3	[85]	$POCl_3$	1.4	[97]
CCl_4	2.0 ± 0.2	[85]	PtF_6	$\geqslant 5.1 \pm 0.5$	[93]
$CFCl_2$	1.1 ± 0.3	[85]	ReF_6	>3.89	[92]
$CFCl_3$	1.1 ± 0.3	[85]	ReF_6	$\geqslant 5.1 \pm 0.5$	[93]
CF_2Cl	1.6 ± 0.3	[85]	SF_3	3.1 ± 0.2	[93]
CF_2Cl_2	0.4 ± 0.3	[85]	SF_4	0.8 ± 0.2	[93]
CF_3	1.9 ± 0.3	[85]	SF_5	2.9 ± 0.1	[98]
CF_3Br	0.9 ± 0.2	[86]	SF_5	2.7 ± 0.2	[93]
CF_3I	1.6 ± 0.2	[86]	SF_6	0.32 ± 0.15	[98]
CF_3I	1.4 ± 0.2	[87]	SF_6	0.46 ± 0.20	[93]
$CHCl_2$	0.0 ± 0.3	[85]	SO_2	1.14 ± 0.15	[96]
CH_3NO_2	0.4 ± 0.2	[86]	SO_3	1.70 ± 0.15	[96]
COS	0.46 ± 0.20	[88]	SbF_6	6.0	[82]
CS_2	1.0 ± 0.2	[88]	SeF_6	2.9 ± 0.2	[93]
CS_2	0.6 ± 0.2	[89]	$SnCl_3$	3.7 ± 0.5	[90]
Cl_2	2.4 ± 0.2	[84]	$SnCl_4$	2.49 ± 0.15	[90]
FCl	1.5 ± 0.3	[85]	TeF_6	3.3 ± 0.2	[93]
$GeCl_3$	>2.61	[90]	$TiCl_4$	2.88 ± 0.15	[90]
HNO_3	0.57 ± 0.15	[91]	UF_5	$\geqslant 1.9$	[94]
IrF_6	>4.34	[92]	UF_5	4.0 ± 0.4	[99]
IrF_6	$\geqslant 5.1 \pm 0.5$	[93]	UF_6	$\geqslant 4.3$	[94]
MoF_5	>3.3	[94]	UF_6	5.1	[99]
MoF_5	$\geqslant 3.5$	[93]	WF_5	1.25	[100]
MoF_6	>3.89	[92]	WF_5	$\geqslant 1.8 \pm 0.3$	[93]
MoF_6	$\geqslant 4.5$	[94]	WF_6	>4.5	[92]
MoF_6	$\geqslant 5.1 \pm 0.5$	[93]	WF_6	$\geqslant 4.9$	[94]
NO_2	2.5	[95]	WF_6	3.7	[99]
			WF_6	5.1 ± 0.5	[93]

* Estimated value.

In the collision of neutral particles the main problem is how to control the energy of the collision. In ion–molecule reactions this problem disappears, since the energy of charged particles is readily controlled by an electrostatic field, but in reactions between neutral particles a special solution of this problem must be found. Two different approaches have been used so far to prepare beams of neutral particles having energies of a few electron volts. The first relies on the application of supersonic flow technologies. The technique has been used[79,80] to study the formation of the ion pairs Cs^+ and Cl^-, Cs_2Cl^+ and Cl^-, and Cs^+ and $CsCl_2^-$ by collisions between the molecules CsCl or Cs_2Cl_2 and the atoms Ar, Kr, Xe (or the molecule SF_6) at energies which could be varied from thermal energy to 18 eV. These very high energies (for neutral particles) were obtained by gas-dynamic methods. No numerical values of the electron affinity of molecules have been obtained by this method so far: one possible reason is the formation of ion pairs at energies well in excess of the threshold energy of the reaction.

The second approach uses ionisation by collisions with alkali metal atoms. "Fast" alkali metal atoms can be obtained by transferring charge from M^+ ions which have been accelerated in an electric field to neutral M atoms. This method can yield atomic beams of alkali metals having a high and controlled (to ~ 0.1 eV) energy. Ionisation by alkali metals is widely used to measure the electron affinity of organic[81] as well as inorganic molecules. The method has been intensively developed by several groups of workers, and in recent years it has yielded important information on electron affinities (Table 4).

VI. EQUILIBRIUM METHODS

The electron affinity can be calculated by measuring the equilibrium constant of the reaction $A^- \rightarrow A + e$ at a known temperature T:

$$K_p = p_A p_e / p_{A^-} ,$$

where p_A, p_e, and p_{A^-} are the partial pressures of A molecules, of electrons, and of A^- ions in the system in thermodynamic equilibrium. The electron affinity, numerically equal to the heat ΔH_0° of the reaction at $T = 0$ K, is calculated by the equation

$$E(A) = \Delta H_0^\circ = RT \ln K_p + \Delta\Phi^\circ ,$$

where $\phi^\circ = S_T^\circ - (H_T^\circ - H_0^\circ)/T$ is the reduced Gibbs energy.

For gaseous molecules and ions the quantity ϕ° can be calculated by statistical thermodynamic methods from molecular constants. Unfortunately, very few data are available on the electronic states, structures, and vibration frequencies of negative ions, and practically none on polyatomic ions. Hence the calculations must be based on estimated molecular parameters, which lowers the precision of the results, but to an acceptable extent, since the entropy of the reaction is relatively insensitive to the uncertainty of the molecular parameters of the reactants and products.

In most cases the error in the estimated entropy of the gas-phase reaction is between 1 and 4 e.u., leading to an error of ~ 0.05–0.20 eV in the estimated electron affinity. The main difficulty in the use of this method lies in establishing an experimental procedure which gives reliable values of the equilibrium constant. Different methods have to be combined in order to obtain simultaneous measurements of the partial pressure of molecules, ions, and electrons. The neutral and the charged particles must be sampled from the same place, where local equilibrium is known to exist. The difficulty of simultaneously measuring the relative pressures of negative ions and electrons was solved by an apparatus which has been called the magnetron[101].

A method which avoids the need to measure the concentration of electrons can be based on surface ionisation, in which two ion currents are measured as a function of the surface temperature of the ion source. The result of this experiment is the difference in electron affinity between two atoms or molecules. If one of the electron affinities is known, the other is easily calculated. The surface ionisation method is widely known, and fully described in Ref.102. The latest developments in surface ionisation techniques in relation to the determination of electron affinities are discussed in Ref.103. The sample is evaporated from the surface of the ion source by means of a beam of positive ions rather than by a molecular beam (as in the conventional form of the method). This improvement offers very good control of the purity of the surface and of the thickness of the evaporated layer. The positive ions are neutralised, and the resulting molecules can undergo electron capture[103].

The most serious shortcomings of the magnetron method and of the surface ionisation method are due to the presence of temperature and concentration gradients between the bulk of the gas phase and the surface of the hot filament, and also to the large variations in the local value of the work function[104], which can lead to incorrect values of the electron affinity[1].

A more direct approach to the measurement of electron affinity relies on measuring the concentrations or pressures of ions, electrons, and molecules in a gas[64,105,106], vapour[107,108], flame[109], or plasma[110,111]. The experimental procedures developed for exploiting the drift of ions in a carrier gas have been used in studies of ion-molecule reactions and of the rate constant of electron removal by a bimolecular reaction such as $O_2^- + O_2 \rightarrow e + 2O_2$[105] or $NO^- + NO \rightarrow e + 2NO$.[106] At the same time the rate constants of the electron capture reactions in three-body collisions (i.e. in the reverse reaction) were also measured. Knowing the rate constants for the forward and the reverse reaction, the equilibrium constant and the electron affinity were calculated for the O_2[105] and the NO molecule[106]. Another example of the determination of equilibrium constants was mentioned in Section III above: the measurement of the rate constants of the forward and the reverse reaction by using ion–cyclotron resonance. The electron affinity of the OCN radical was calculated[64] from the equilibrium constant measured in this way.

Table 5. Electron affinities determined by measuring the equilibrium constants of ion–molecule reactions.

Molecule	E, eV	Reference	Molecule	E, eV	Reference
BO	$\geqslant$2.49	[109]	PO_2	3.0	[110]
BO_2	4.07±0.21	[109.112]	PO_3	3.5	[110]
CeF_4	3.6±0.3	[124]	PtF_4	5.25±0.20	[128]
CrO_3	2.38±0.52	[109.144]	PtF_5	6.5	[128]
FeF_3	4.25±0.20	[124]	PtF_6	8.0±0.3	[126]
FeF_4	5.40±0.20	[124]	ReO_3	2.85±0.55	[109]
FeO_2	2.85	[110]	ReO_4	4.45	[115]
$HCrO_3$	4.04±0.52	[109.114]	UF_5	3.30±0.16	[129]
$HMoO_4$	4.25	[109.176]	UF_6	4.89±0.25	[129]
HWO_4	4.15	[109.113]	WF_6	5.5	[111]
MnF_2	4.36±0.15	[127]	WO_3	3.64±0.41	[109.113]
MnF_3	5.27±0.20	[128]	WO_2	3.6	[111]
MoO_3	2.58±0.41	[109.116]	MoF_5	3.63±0.20	[72]
PO_2	3.68±0.41	[115]	MoF_6	3.68±0.20	[72]

A series of papers[112–116] describes ion–molecule equilibrium studies in flames consisting of hydrogen, nitrogen, and oxygen. The aim of the work was to study electron capture processes by additives assumed to have a very high electron affinity. Tungsten was introduced into the flame as $W(CO)_6$ or WF_6, chromium as $Cr(NO_3)_3$ or $Cr(CO)_6$, and rhenium as an aqueous solution of a rhenium salt or as ReF_6. Atomic potassium or caesium were also added as electron donors. The experiment consisted in measuring the equilibrium constants of the reactions involving molecules, ions, and electrons:

$$e + H_2WO_4 \rightarrow HWO_4^- + H$$

$$HWO_4^- + H \rightarrow WO_3^- + H_2O$$

$$WO_3 + e \rightarrow WO_3^- .$$

The concentrations of negative ions and of electrons were determined with a mass spectrometer and microwave resonator; the concentrations of neutral molecules or atoms were

calculated from standard thermodynamic formulae by using the heat of formation and the total concentration of the additive (i.e. the weights of chromium, molybdenum, tungsten, or rhenium introduced). From the equilibrium constants obtained in this way the heats of the reactions and the heats of formation of the negative ions were calculated. The electron affinities were determined as the difference between the heats of formation of the negative ion and those of the corresponding neutral molecule. The results are given in Table 5.

Some recent attempts to study electron affinities by measuring the electrical conductivity of plasmas have been reported[110-111]. The method depends on the large decrease in the electrical conductivity of the plasma caused by the formation of molecules and radicals with a high electron affinity. Model calculations suggest that the decrease can be as high as 10–40%, depending on the type and concentration of the additive: for example, oxides of iron, aluminium, and phosphorus lead to the formation of the ions FeO_2^-, PO_2^-, PO_3^-, and AlO_2^-.[110] The electrical conductivity of the plasma has been measured[111] as a function of the type and concentration of the additives. We see from the results (Table 5) that some hexafluorides have extremely high electron affinities (~ 5 eV).

The effusion method was first used in 1971–1974 to measure electron affinities[107,108,117] by studying the equilibrium between negative ions and neutral molecules in a Knudsen cell. The cell had to be heated to ~ 2000 K in order to give measurable concentrations of negative ions. The experimental substances were placed (at lower temperatures) in separate temperature-controlled compartments. By heating these compartments the experimental substances were transferred through connecting channels to the mixing chamber, where they underwent partial dissociation into neutral particles and charged particles. The neutral particles were monitored by conventional high-temperature mass spectroscopic methods. The negative ions present in the vapour of the experimental substances were also monitored mass spectroscopically after being "extracted" from the effusion cell by an electrostatic field.

Table 6. Heats (ΔH°_{298}) of the gas-phase reaction $MF_n + F^- = MF_{n+1}^-$.

Molecule	$-\Delta H^0_{298}$, eV	Reference
AlF_3	5.16±0.10	[120,123,130]
BeF_2	4.07±0.19	[131]
CeF_3	4.76±0.09	[124]
FeF_2	4.57±0.11	[124,132]
FeF_3	4.55±0.10	[124,132]
HfF_4	4.22±0.09	[131]
KF	2.26±0.06	[133]
LaF_3*	4.94±0.35	[122]
MnF_2	4.45±0.13	[124,132]
MnF_3	4.55±0.13	[124,132]
ScF_3	5.05±0.13	[133]
UF_4	4.26±0.09	[130]
UF_5	4.83±0.35*	[122]
ZrF_4	4.23±0.13	[124]

* Calculated from published data[122].

The equilibrium constants of several ion–molecule reactions involving negative ions were successfully measured, and the electron affinity (eV) of the following molecules and radicals was determined: AlF_2 (2.30), BF_2 (2.20)[117]; BO (3.12), BO_2 (3.47)[107]; AlO (3.68), AlO_2 (4.11).[108] It was subsequently discovered that the use of very high temperatures (2000–2500 K) to obtain measurable concentrations of negative ions is not essential.

Negative ions were detected in the saturated vapour of a large number of inorganic salts and their binary systems at temperatures as low as 700–1200 K.[118-122] This observation led to the rapid development of studies of ion–molecule equilibria and to the determination of affinities for the electron and for the F^- anion. Many workers[110-123] have reported experimental tests of the existence of ion–molecule equilibrium under the conditions of a real effusion experiment and have developed methods of measuring the activity of neutral components from measurements of the partial pressures of negative ions. The fullest description of these techniques is given in Ref. 124 and 125, where the effect of the extracting field on the effusion process and on the electronic work function of the inner surface of the effusion cell is also discussed.

In the last two or three years the effusion method has been used to measure the affinity for the electron and for the F^- anion of a large number of inorganic fluorides (Tables 5 and 6). The most important of these results was the first experimental determination of the electron affinity of platinum hexafluoride: the highest electron affinity ever reported[126].

VII. CALCULATION OF ELECTRON AFFINITY FROM THERMOCHEMICAL DATA AND FROM THE ABSORPTION SPECTRA OF COMPLEXES

The difficulty of the direct experimental determination of electron affinity has led to the development of several methods by which the electron affinity can be estimated from measurements of related quantities. Typical of this approach is the calculation by a Born–Haber thermochemical cycle in which reactions involving both the charged and the neutral particles are included.

In order to calculate the electron affinity by this cycle we need to measure the heat of formation $\Delta H^\circ_{0f}(AB)$ of the crystalline compound AB from the gaseous components A and B, and to calculate theoretically the crystal lattice energy U of the compound. The energy U is equal to the heat of reaction (1) ($U = -\Delta H^\circ_0(1)$):

$$A^+(g) + B^-(g) \rightarrow Ab(cr) . \quad (1)$$

The heat of formation of the crystalline compound AB from gaseous A and B is equal to the heat of reaction (2), $\Delta H^\circ_0(2)$:

$$A(g) + B(g) \rightarrow AB(cr) . \quad (2)$$

The electron removal and addition reactions are written

$$A \rightarrow A^+ + e \quad (\Delta H^0_0(3) = I(A)) , \quad (3)$$

$$B + e \rightarrow B^- \quad (\Delta H^0_0(4) = -E(B)) , \quad (4)$$

where $I(A)$ is the ionisation energy (potential) of A and $E(B)$ is the electron affinity of B. The ionisation energy is usually known, and the electron affinity is calculated as the algebraic sum of the heats of reactions(1), (2), and (3):

$$\Delta H^0_0(4) = \Delta H^0_0(2) - \Delta H^0_0(1) - \Delta H^0_0(3) \quad (5)$$

or

$$E(B) = I(A) - U - \Delta H^0_0(2) .$$

Measurements of the heats of formation of molybdenum and tungsten pentafluorides and of the complexes MWF_6 and $MMoF_6$ (where M = Li–Cs) have been reported[134-136]. The crystal lattice parameters were determined, and used to calculate the energy of formation of crystalline MWF_6 and $MMoF_6$ from the M^+ and MoF_6^- (or WF_6^-) ions. By combining

the results with the known heats of formation of the pentafluorides, the electron affinities of the hexafluorides and the affinities for the F^- anion of the pentafluorides were calculated. In a more recent paper[136] an improved calculation of the crystal lattice energy is presented and a slightly different value of the electron affinity is obtained (see Table 7).

Table 7. Electron affinities calculated from thermochemical and spectral data.

Molecule	*E*, eV	Reference
HO_2	1.85±0.12	[138]
IBr_2	4.94	[139]
ICl_2	5.35	[139]
ICl_4	3.98	[139]
I_3	5.27	[139]
IrF_6	7.85 (6.8)*	[137]
MoF_6	5.36±0.06	[134]
MoF_6	5.77 (4.8)*	[137]
ReF_6	<6.33 (5.3 *	[137]
UF_6	<5.81 (4.8)*	[137]
WF_6	5.08±0.05	[134]
WF_6	4.63	[136]
WF_6	4.51 (3.5)*	[137]

* Calculated from the absorption spectra of the complexes by using the most recent value[62] of the electron affinity of WF_6; $E(WF_6) = 3.5$ eV. The other entries are thermochemical calculations.

The first attempt to calculate the electron affinities of the transition metal (W, Mo, U, Re, Ir) hexafluorides from the absorption spectra of their complexes was reported[137] in 1978. New frequencies were observed in the visible and near u.v. regions of the absorption spectra of the crystals formed by the hexafluorides with xenon at liquid-nitrogen temperatures. They were assigned to intermolecular charge transfer between xenon and the hexafluoride:

$$Xe + MF_6 \xrightarrow{h\nu} Xe + MF_6^- .$$

The theory of charge transfer in complexes[13] leads to the expression

$$h\nu = I(Xe) - E(MF_6) + G ,$$

where $I(Xe)$ is the ionisation potential of the donor (Xe), $E(MF_6)$ is the electron affinity of the acceptor (MF_6), and G is a constant determined empirically by using a standard ($XeWF_6$ crystals). The energy $h\nu$ was determined experimentally, and the constant G was calculated by combining this value with published data on the ionisation potential of xenon and on the electron affinity of tungsten hexafluoride. From the G value, and the measured charge transfer frequencies of the xenon complexes, the electron affinities of five hexafluorides were calculated (Table 7). We note that the most recent value[62] of $E(WF_6)$ is 3.5 ± 0.1 eV, whereas the value 4.5 eV was used in Ref.137. Therefore all the results quoted in that paper should be lowered by ~ 1 eV.

VIII. COMPOUNDS HAVING AN ELECTRON AFFINITY GREATER THAN 3.0 eV

Each of our Tables (1–7) includes electron affinity values measured by one particular method. By comparing these results we can assess the relative merits of different approaches to the problems presented by the study of molecules with a high electron affinity.

Photo-extraction occupies a leading place among existing experimental methods of measuring electron affinity, and no other method can compete with the precision of its results. Measurements by negative ion photo-electron spectroscopy are usually claimed to have a precision of 0.01–0.02 eV, and in some cases (for example, for the carbon atom) the precision is as high as 0.0003 eV.[16] In photo-extraction experiments where the percentage breakdown of the anions is fixed a precision of 0.02–0.10 eV is usually quoted. The results are more difficult to interpret, since allowance is needed for the difference in energy between adiabatic and vertical transitions. Negative ion photo-electron spectroscopy gives a direct measurement of the lowest photon energy capable of generating a free electron. This energy corresponds to a vertical transition and is higher than the energy of the adiabatic transition which is equal (by definition) to the electron affinity. The numerical importance of these differences can be assessed only by comparing the results with those obtained by independent methods.

The photo-electron spectroscopy method can also be used to determine the enthalpies of formation of gaseous compounds having a high electron affinity. These compounds readily form stable negative ions in the gas phase, and it is experimentally easier to determine the enthalpy of formation of the negative ion than that of the corresponding neutral molecule or radical. Many examples can be quoted, and in some cases (e.g. AlF_4^- and HfF_4^- (Table 6), WF_7^- (Ref.62), and UF_7^- (Ref.63)) the enthalpy of formation of the negative ion is reliably determined while the existence of the corresponding neutral radical remains doubtful. Evidently, the enthalpy of formation of these radicals could be determined from measurements of the enthalpy of formation of the negative ions and the energy of extraction of an electron.

Consider the CO_3 molecule and the CO_3^- ion. The bond energy $D(O_2C-O^-)$ for the ion is accurately known, the most recent value[29] being 2.258 ± 0.007 eV. The electron affinity of the oxygen atom is known[5] to an even higher accuracy: $E(O) = 1.462 \pm 0.003$ eV. For the neutral CO_3 molecule the bond energy data are less reliable: $D(O_2C-O) = 0.46 \pm 0.17$ eV.[140] Since $E(CO_3) = D(CO_2-O^-) + E(O) - D(O_2C-O)$, we obtain $E(CO_3) = 3.26 \pm 0.17$ eV. Direct determination of the electron affinity by the negative ion photo-electron spectroscopy method should give a value of $E(CO_3)$ accurate to a few hundredths of an electron volt, and therefore a back-calculation should give a better value of the bond energy $D(O_2C-O)$ for the molecule. Unfortunately, the first attempt was unsuccessful[35], possibly because the intensity of the CO_3^- beam was insufficient, and the photo energy was adequate only for electron affinities lower than 3.1 eV.

There is little doubt that increasing the photo energy should provide the desired result and give more accurate values not only of the electron affinity but also of the heat of formation of the CO_3 molecule. Unfortunately, up to the present all the results obtained by the photo-extraction method lie between 0 and 3 eV (see Table 1). There are no fundamental obstacles to an extension of the measurements to higher energies, though of course some practical difficulties can be expected. The further development of the photo-extraction method and its application to the study of molecules with a high electron affinity should increase very substantially our understanding of the thermochemistry of negative ions and that of their related molecules and radicals.

The electron impact method occupies the second place in relation to the number of results obtained (see Table 2). Nearly all the results were derived from the appearance potentials of negative ions during dissociative electron capture

processes involving the molecules of interest. Inspection of Table 2 shows that in most cases uncertainty limits are not quoted, and occasionally only an upper limit is given. Some results obtained by the electron impact method have been criticised by Mathur and coworkers[90]. The dissociative electron capture method is applicable to the determination of electron affinity in compounds of higher valency only if the molecules undergoing ionisation are even more complex, e.g. $KMoF_6$ or KWF_6. In this case the electron affinity of MF_6 can be determined if MF_6^- ions are formed by dissociative electron capture. Unfortunately, no such results have yet been reported, and an attempt to prepare the AlF_4^- ion by dissociative electron capture from the $NaAlF_4$ molecule was unsuccessful.

Studies of ion–molecule reactions (Section IV) have revealed only 10 substances with an electron affinity higher than 3 eV. The affinity was calculated from the threshold energy of an endothermic ion–molecule reaction[59,61], from the threshold energies of two exothermic ion–molecule reactions[62], or by measuring the rates of the forward and the reverse reaction, i.e. from the equilibrium constant[64]. The latter variant is considered in Section VI, devoted to equilibrium methods. Studies of ion–molecule reactions have yielded relatively few electron affinity data, and the precision of the results usually lies in the range 0.1–0.3 eV (see Table 3).

Relatively few studies of ion–molecule reactions involving negative ions had been reported until recently. The limitation lay both in the method of producing negative ions and in the inadequacy of the available thermochemical data (mainly, on heats of formation). The position has shown a marked improvement in recent years, with a rapid increase in the number of negative ions which can be obtained in the gas phase and in the list of known heats of formation. A good example are the anions (Table 6) which are easily formed by heat treatment of complex salts of the $MAlF_4$ type, where M is an alkali metal[120]. The use of these anions in studies of endothermic ion–molecule reactions should make an important contribution to the acquisition of thermochemical data on fluorine compounds.

In Section V we examine a method based on the formation of an ion pair by the collision of a molecule with an alkali metal atom. Ionisation can be induced by collisions with Cs, K, and Na atoms, and the upper limit of the electron affinities measurable by this method is 5.14 eV, i.e. the ionisation potential of the sodium atom. There is effectively no lower limit. During the last 5 years this method has yielded the greatest number of results: 73 affinity values, 21 of which were higher than 3.0 eV. The method is being actively developed by several groups of workers (see Table 4), who claim a precision between 0.15 and 0.30 eV. There are a number of inconsistencies between the results reported from German and American laboratories, for example in the case of WF_6[93,100]. The high values of the internal excitation energy are surprising.[141] Unfortunately, for most of the hexafluorides the electron affinity is only given as "higher than 5.14 eV", since negative MF_6^- ions are formed even from sodium atoms at thermal energies.

The determination of thermochemical quantities from the absolute values of the equilibrium constants is one of the main experimental methods of chemical thermodynamics. In studies of equilibria involving the gas phase this is one of the principal methods, giving heats of reaction accurate to ~ 4–12 kJ $mole^{-1}$ (0.05–0.15 eV). Therefore experimental methods of measuring the constants of ion–molecule equilibria involving negative ions have been intensively developed during the past 10 years, including work on flames[109], plasmas[110,111], and on the formation of clusters on negative ions[142,143].

The application of the classical effusion method to these problems had only limited success at first, because of the high value of the work function of the inner surface of the Knudsen effusion cell and of the low concentration of negative ions[144]. However, in the case of molecules with a high electron affinity (i.e. for $E > 3$ eV) these problems are less important. A method of lowering the work function of the inner surface of the Knudsen cell during the effusion measurement was also discovered[125]. As a result, the effusion method can now be used to measure electron affinities $E > 3$ eV, and work now in progress may result in a lowering of this limit. The method has no upper limit, since the higher the electron affinity, the easier it is to obtain measurable concentrations of negative ions in the effusion cell.

During the period 1979–1981 this method has been used to determine the electron affinities of iron, manganese, platinum, uranium, and cerium fluorides, and the affinities for the F^- anion of a series of fluorides (see Table 6). The precision of the results is 0.1–0.3 eV, and is often limited by the uncertainty in the heats of formation of the corresponding neutral compounds. The range of substances suitable for investigation by this method can easily be widened to include other halides, oxide halides, oxides, and salts of oxygenated acids. This type of measurement can yield the affinity for other anions as well as the electron affinity. For example, the affinities of the BeF_2 molecule for the following anions have been measured[131]: F^-, BeF_3^-, $Be_2F_5^-$, AlF_4^-, and $BeAlF_6^-$. This work has much in common with the study of cluster formation on negative ions by the method which has been called high-pressure mass spectrometry[142]. Keesel and coworkers[142] determined the heats of formation of $A(SO_2)_n$ clusters on A ions (Cl^-, I^-, NO_2^-), with $n = 1$–4, and Nikitin and coworkers[131] determined the heats of formation of $F^-(BeF_2)_n$ clusters, where $n = 1$, 2, and 3.

We note that the Knudsen effusion cell in addition to its normal purpose (the generation of equilibrium conditions) can also be used as an efficient source of negative ions in methods such as photo-extraction, photo-electron spectroscopy, and other threshold methods of determining electron affinities. When used as an ion source the effusion cell offers the simplest way of applying such methods to the study of those negative ions, which play an important role in high-temperature systems.

The methods discussed in Section VII occupy a special position, because they cannot be classified among the direct experimental methods of determining electron affinities, and they are used mainly to obtain approximate estimates of the affinities. For this reason the results quoted in Table 7 are only tentative, but they are nevertheless of interest because of the increasing importance of this class of compounds in investigations of the reality of electron affinity values in the range 4–8 eV. At present the following values have been reliably established:

Molecule	WF_6	MoF_6	UF_6
E, eV	3.5 ± 0.1 [62] 3.7 ± 0.2 [100] 4.89 ± 0.25 [129]	3.6 ± 0.2 [72]	4.9 ± 0.5 [63] $\geqslant 5.14$ [99]

By comparing these values with those of Table 7 we note discrepancies often greater than 1 eV. The most serious inconsistencies arise with the data obtained from the absorption spectra of complexes. The disagreement affects not only the absolute values of electron affinities (which could be due to an incorrect choice of standard) but also their differences: for example, the difference $E(MoF_6) - E(WF_6)$ according to these data is 1.3 eV, as compared with only 0.1–0.3 eV according to the results obtained by other methods. We conclude that the data of Table 7 should only be used as a rough estimate of the electron affinity, with a precision not better than ~ 1.5 eV.

The experimental results summarised in Tables 1–7 characterise the electron affinity of a large number of inorganic molecules and allow us to identify the classes of compounds for which numerical values of the electron affinity higher than those of the halogen atoms can be expected. Inspection of Table 5 shows that higher-valency oxygen compounds have an electron affinity in the range 3.5–4.3 eV (the BO_2, PO_3, WO_3, HWO_4, $HMoO_4$, and ReO_4 radicals). Even higher values (5.25–5.40 eV) are obtained for the tetrafluorides of the transition metals (FeF_4, MnF_4, PtF_4). Measurements on cerium tetrafluoride gave a value of 3.6 eV, believed to be typical of the tetrafluorides of the lanthanum group. Still higher values were obtained in studies of the hexafluorides.

Bartlett's prediction[145], made in 1968, has been confirmed experimentally: the electron affinities of all the hexafluorides of transition metals in the second and the third series are higher than 3.5 eV, and in the case of platinum hexafluoride the electron affinity is higher than 6.8 eV. According to existing data, $E(PtF_6) = 8.0 \pm 0.3$ eV.[126] For the ReF_6 and IrF_6 molecules the reported value is $E > 5.14$ eV, and for WF_6 and MoF_6 values of 3.5,[62] 3.7,[100] and 3.6 eV[72] have been obtained. Hence the higher fluorides (and probably also the oxide fluorides) of the second and third series of transition metals are a class of compounds showing the highest electron affinity values so far reported. Uranium hexafluoride has an electron affinity of ~ 5 eV, and similar values can be expected for the hexafluorides of the transuranic elements. The high values of electron affinity in this class of compounds probably persist in halides (and oxide halides) other than the fluorides.

The data in Table 6 can be used to calculate the enthalpies of formation of the negative ions BeF_3^-, AlF_4^-, ScF_4^-, LaF_4^-, ZrF_5^-, and HfF_5^-. Similar data are available for the anions WF_7^-[69] and UF_7^-.[63] For the UF_7 radical the energy of addition of the seventh fluorine atom is positive[63], i.e. the potential energy curve of the UF_6–F system has a minimum. For the AlF_4, ScF_4, LaF_4, ZrF_5, HfF_5, and WF_7 radicals this information is not yet available, and the minimum in the potential energy curve may be absent in some of the systems. The enthalpies of formation of these radicals are not known, and only a rough estimate of their electron affinity is possible (5–8 eV[147,149]). Some estimates suggest even higher values of the electron affinity: the record is held by gold hexafluoride, for which a value of 10 eV has been proposed[93]. Of course, there are no direct experimental data, and the compound itself has not yet been synthesised. An analogous situation exists in many instances of high (expected) electron affinity. A good example are the hexafluorides of iron, cobalt, and nickel, whose synthesis has not yet been achieved in spite of repeated attempts.

The compounds with a high electron affinity are the strongest known oxidising agents. They have a strong influence on the concentration of free electrons in flames and plasmas, and they greatly simplify the problem of generating strong beams of negative ions.

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New information on the affinity of compounds for electrons and for the F^- ion has appeared while the manuscript was being prepared for the press.

Photo-extraction and photo-electron spectroscopy methods have been used to obtain the electron affinities of the following compounds: $E(CH_2) = 1.055 \pm 0.0 \pm 5$,[148] $3.374 \leq E(C_2) \leq 3.408$,[166] $E(HO_2) = 1.19 \pm 0.01$,[150] $E(HS) = 2.314 \pm 0.003$ eV.[151] In addition to these experimental papers, a review entitled "Laser spectroscopy of negative ion beams" has also appeared[152]. The electron impact method has been used to show that $E(OF) \geq 2.2$, $E(NF) \cong 0.5$, $E(ClO_3) \geq 3.2$, $E(ClO_2F) \geq 2.3$ eV,[153] and also $E(CCl_2) = 2.5 \pm 0.3$ and $E(CCl_3) = 2.58 \pm 0.20$ eV.[154]

Studies of endothermic ion–molecule reactions have yielded values of the affinity for the electron and for the fluoride anion (E_F^-), and also of the energy of the removal of an oxide anion ($D(MO_n-O^-)$): $E(SF_5) \geq 3.70 \pm 0.3$, $E_F^-(SF_3) = 2.60 \pm 0.16$, $E_F^-(SF_4) \geq 2.60 \pm 0.16$, $E_F^-(SF_5) = 1.10 \pm 0.21$[155]; $D(N-O^-) = 5.0 \pm 0.1$, $E(NO) = 0.02 \pm 0.10$, $D(O-O^-) = 4.1 \pm 0.1$, $E(O_2) = 0.44 \pm 0.1$, $D(NO-O^-) = 4.0 \pm 0.1$, $E(NO_2) = 2.4 \pm 0.1$, $D(N_2-O^-) = 0.43 \pm 0.1$, $E(N_2O) = 0.22 \pm 0.1$, $D(CO_2-O^-) = 2.0 \pm 0.1$, and $E(CO_3) = 3.1 \pm 0.2$ eV.[156]

Ionisation by potassium atoms has been used to prepare negative D_2S^- and H_2S^- ions. The corresponding values of the electron affinity were found to be negative: $E(D_2S) = -1.5 \pm 0.2$ eV and $E(H_2S) = -1.6 \pm 0.2$.[157]

Measurements of the equilibrium constant of ion–molecule reactions have yielded additional information on the thermochemical characteristics of negative ions. Pyatenko and coworkers[158] have obtained $E(UF_5) = 3.78 \pm 0.40$ and $E(UF_6) = 6.33 \pm 0.50$ eV, and Chilingarov and coworkers[159] reported $E(RhF_4) = 5.0 \pm 0.3$ eV. The affinity for the F^- anion was measured, with the following results: $E_F^-(LaF_3) = 4.42$,[160] $E_F^-(VF_3) = 4.9 \pm 0.1$,[161] and $E_F^-(ThF_4) = 4.2 \pm 0.1$ eV.[162] Similar measurements have been reported also for the oxide fluorides of molybdenum and tungsten: $E_F^-(MoO_2F_2) = 4.08 \pm 0.17$ and $E_F^-(WO_2F_2) = 4.30 \pm 0.17$ eV.[163] A detailed description of the determination of the electron affinity of cerium tetrafluoride (including the procedure) is given in Ref. 165. It is interesting to compare these results with experimental data for the hexafluorides of molybdenum[72], tungsten[62], and platinum[126]. These experimental and theoretical results were obtained, independently, in the period 1979–1981, and it is very instructive to compare them with earlier data.

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The Synthesis of Substituted Cyclopropanes and Cyclopropenes by the Reductive Cyclisation of Polychloroalkanes

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The methods of synthesis of three-carbon rings—substituted cyclopropanes and cyclopropenes, obtained by the action of various metals on polychloroalkanes with chlorine-containing groups in the 1,3-positions relative to one another, are reviewed. Reductive cyclisation with zinc of compounds having the groups $-CCl_2CH_2CCl<$ or $CCl_3CH_2CCl<$ gives rise to new possibilities for the synthesis of substituted cyclopropanes. A new method of synthesising 1,2-disubstituted cyclopropenes from compounds with the group $-CCl_2CH_2CCl_2$ is examined.

The bibliography includes 87 references.

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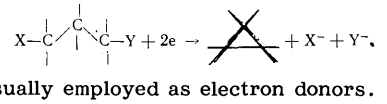
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I. INTRODUCTION

The chemistry of compounds of the cyclopropane and cyclopropene series has attracted the constant attention of investigators. This is indicated particularly by the appearance of annual reviews of literature on the synthesis of these compounds[1-8]. During recent years, reviews have been published on individual methods of synthesis of substituted cyclopropanes: the carbene method[9,10], the Simmons–Smith method[11], synthesis with the aid of the copper-isonitrile complex[12,13], and the electrochemical method[14,15]. Cyclopropene compounds are usually obtained by β-elimination from halogenocyclopropanes, by the addition of carbenes to acetylenes, or by the intramolecular cyclisation of the corresponding unsaturated aliphatic compounds[16,17]. Reviews have been devoted to the properties and reactions of three-carbon rings[18-32].

The structures of these rings have been confirmed by infrared, Raman, and ^1H NMR spectroscopy[33-35]. ^{13}C NMR has been used with an increasing frequency in recent years for the solution of problems of the structure of cyclopropanes[36-40]. cyclopropanes with an exocyclic double bond[41,42], or cyclopropenes[43-45].

Among the numerous methods for the synthesis of three-carbon rings, our attention was attracted to the intramolecular cyclisation of aliphatic chloro-compounds, particularly the 1,3-elimination (or γ-elimination) reaction[46] involving the removal of two halogen atoms with formation of a new C–C bond. The 1,3-dehalogenation reaction permits the direct conversion of an aliphatic halogenohydrocarbon into cyclopropane homologues with the same number of carbon atoms. The stoichiometry of this process is represented by the following equation in a general form:



Metals are usually employed as electron donors.

The aim of the present review is a survey of studies devoted to the synthesis of three-carbon rings from polychloroalkanes with chlorine-containing groups in the 1,3-positions relative to one another. Examples of such reactions have been mentioned in certain reviews, but they have never been surveyed and examined from the standpoint of their suitability for the synthesis of compounds of cyclopropane and cyclopropene series. Furthermore, new possibilities for the synthesis of a wide variety of cyclopropanes and cyclopropenes by reductive 1,3-dechlorination have been discovered in recent years, which necessitates a special discussion of all the results concerning this field. This review deals with the literature data published up to January, 1981.

II. 1,3-DECHLORINATION OF DICHLOROALKANES AND DICHLOROALKENES

The synthesis of cyclopropane by the 1,3-dechlorination of 1,3-dibromopropane by sodium was first described by Freund[47]. Gustavson[48] showed that the application of zinc dust in alcohol as the dehalogenating agent is more convenient. Subsequently it was found that the Gustavson 1,3-dehalogenation is of general importance for the synthesis of compounds of the cyclopropane series[49,50]. However, it was discovered that, whereas the use of 1,3-dibromoderivatives gives rise to satisfactory results, 1,3-dichloroderivatives are less valuable[50,51].

Without dwelling on numerous examples of the synthesis of substituted cyclopropanes from 1,3-dibromo-compounds, we shall consider below the 1,3-elimination of chlorine from organic polychloro-compounds.

Table 1 presents all the examples of the synthesis of cyclopropane and cyclopropene derivatives from 1,3-dichloro-compounds known at the present time. It is seen that, in order to achieve a high yield of cyclopropane, Na_2CO_3 and NaI have been added[52] to the 1,3-dichloropropane (see No.1 in Table 1), coverting thereby the dichloro-compound into the more reactive di-iodo-derivative. n-Pentylcyclopropane has been obtained by the same method from 1,3-dichlorooctane (Table 1, No.6). It has been observed[54] that satisfactory results are obtained when 1,3-dichloropropane or 1,3-dichlorobutane is treated with the $Cr(ClO_4)_2$-ethylenediamine complex (Table 1, Nos.4 and 5).

Magnesium in tetrahydrofuran can also be used successfully as the dechlorinating agent (Table 1, Nos.8 and 9). It has been shown[57] that the configuration of the dichloro-compound

is very important in the dechlorination of bicyclic systems. Thus the 1,3-dechlorination of *anti*-8-*exo*-4-dichlorodibenzobicyclo[3.2.1]octadiene proceeds with formation of the cyclopropane ring (Table 1, No.9), while in the case of *syn-exo*- and *syn-endo*-dichloro-compounds the benzyl chlorine undergoes hydrogenolysis. The replacement of chlorine by hydrogen occurs also when the zinc–copper[57] or sodium–potassium[62] alloy is used as the dechlorinating agent. Furthermore, on treatment with sodium in ethanol, the dibromo-compound of analogous structure gives rise to a high yield of a hydrocarbon containing the cyclopropane ring[62]. Table 1 presents also examples (Nos.3, 7, 10, and 11) for which 1,3-dichlorination by a wide variety of reducing agents proceeds with low yields of cyclopropane derivatives.

Proceeding to the synthesis of substituted cyclopropenes or their isomers with an exocyclic double bond from unsaturated 1,3-dichloro-compounds, one must note that attempts to obtain methylenecyclopropane by the dechlorination of 3-chloro-2-chloromethyl-1-propene by zinc proved unsuccessful[63]. The use of magnesium as the dechlorinating agent led to the formation of methylenecyclopropane in a low yield (Table 1, No.12). The electrochemical dechlorination of 1,3-dichloroalkenes, leading to substituted cyclopropenes (Table 1, No.13), has been achieved. Birch reduction, leading to cyclic compounds containing the 1,2,3-trichloroalkenyl group and a ring larger than that of cyclohexene, proceeds as reductive dechlorination with formation of bicyclo[*n*.1.0]alkanes (Table 1, No.14).

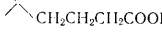
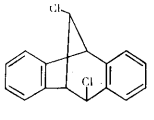
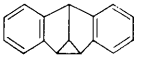
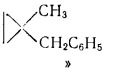
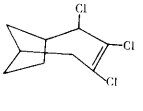
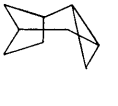
In conclusion of the examination of the 1,3-dechlorination of dichloroalkanes and dichloroalkenes, one should note that these reactions have been achieved in relation to a small number of examples and only some are suitable for the synthesis of three-carbon rings on a preparative scale; in the reviews published recently[7,8] the method of synthesis of three-carbon rings by 1,3-dechlorination is not mentioned at all. 1,3-Dichloro-derivatives containing functional groups are also without importance for the synthesis of cyclopropanes with functional substituents[64].

III. 1,3-DECHLORINATION OF COMPOUNDS WITH THE GROUPS $CCl_3CH_2CCl<$ or $-CCl_2CH_2CCl<$

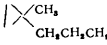
1. The Interaction of Polychloroalkanes with $LiAlH_4$ and CH_3Li; Electrochemical Dechlorination

The 1,3-dechlorination of polychloroalkanes containing the $CCl_3CH_2CCl<$ or $-CCl_2CH_2CCl<$ groups by $LiAlH_4$ and CH_3Li or electrochemically, which leads to compounds of the cyclopropane series, has been described in relation to isolated examples. Thus treatment of 1,1,1,3-tetrachloro- or 1,1,1,3-trichloro-octane with $LiAlH_4$ in dioxan has been

Table 1. 1,3-Dechlorination of dichloroalkanes and dichloroalkenes.

№	Initial compound	Reductant	Solvent	Cyclopropane derivatives	Yield, %	References
1	$ClCH_2CH_2CH_2Cl$	Zn, NaI + Na_2CO_3	C_2H_5OH/H_2O**		95	[52]
2	$ClCH_2CH_2CH_2Cl$	Na	$(C_6H_5)_2O$	»	64	[52]
3	$ClCH_2CH_2CH_2Cl$	Ti	—	»	14	[53]
4	$ClCH_2CH_2CH_2Cl$	Cr^{II}en***	DMF/H_2O	»	86	[54]
5	$CH_3CHClCH_2CH_2Cl$	Cr^{II}en	DMF/H_2O		94	[54]
6	$ClCH_2CH_2CHClC_5H_{11}$	Zn, NaI + Na_2CO_3	C_2H_5OH/H_2O		39	[55]
7	$ClCH_2CH_2CHClC_5H_{11}$	$LiAlH_4$	dioxan	»	—	[55]
8	$ClCH_2CH_2CH_2C(CH_3)(CH_2Cl)_2$	Mg	THF		68	[56]
9		Mg	THF		94	[57]
10	$C_6H_5CH_2C(CH_3)(CH_2Cl)_2$	$LiAlH_4$	dioxan		18	[58]
11	$C_6H_5CH_2C(CH_3)(CH_2Cl)_2$	$LiAlH_4$	THF	»	4	[58]
12	$CH_2=C(CH_2Cl)_2$	Mg	THF		17	[59]
13	$R_2CClCH=CHCl$*****	electrochemically	DMF		—	[60]
14		Na	NH_3 (liq.)		55	[61]

*Here and in the other tables the yields are expressed as percentages of the theoretical yield.
**When the reaction was carried out in CH_3CONH_2 the yield of cyclopropane was 80%.
***en = $NH_2(CH_2)_2NH_2$.
****The product is formed by the carbonylation of the Grignard reagent obtained from



*****Analogous products have also been obtained from $R_2C = CHCHX_2$ (R = CH_3 or C_6H_5).

found to result in the formation of n-pentylcyclopropane (up to 22%) together with the main reaction product—n-octane:[55]

$$XCCl_2CH_2CHClC_5H_{11} \xrightarrow[\text{dioxan}]{LiAlH_4} n\text{-}C_8H_{18} + \triangleright\!-C_5H_{11}\ .$$
X=H, Cl

The electrolysis of CCl_4 or ethyltrichloroacetate in the presence of compounds with polar double bonds (acrylonitrile, ethyl acrylate, etc.) can be classified as cyclisation with participation of geminal polyhalogenoalkyl groups[65]. Electrolysis at a mercury cathode leads to the two-electron cleavage of the added component. The anion, generated electrochemically, attacks the monomer with formation of the anionic adduct (I). The latter is converted into products via several pathways in accordance with the following scheme:

$$(C_2H_5CO_2CCl_2)^- + CH_2{=}CHX \rightarrow (C_2H_5CO_2CCl_2CH_2CHX)^- \rightarrow$$
$$\xrightarrow{a} C_2H_5CO_2CCl_2CH_2CH_2X$$
$$\xrightarrow{b} \text{Cl, } CO_2C_2H_5\text{-substituted cyclopropane, X}$$
$$\xrightarrow{c} C_2H_5CO_2CCl_2CH_2CHClX\ ;$$
X=CN, $CO_2C_2H_5$.

Stage *a* involves the protonation of the anionic adduct (I), stage *b* involves its cyclisation, including the intramolecular substitution of the halogen, and stage *c* involves the abstraction of the halogen from the initial polyhalogeno-compound. This reaction, carried out in dimethylformamide (DMF) in the presence of lithium chloride at room temperature, leads to a substituted cyclopropane (80%) and an adduct (20%). It must be emphasised that under the given conditions the second chlorine atom of the *gem*-dichloromethylene group is retained.

Mixed polyhalogeno-compounds containing chlorine and bromine, such as $CHBr_2CH_2CH_2Cl$ or $CHClBrCH_2CH_2Br$, undergo 1,3-dehalogenation by methyl-lithium[66]. Cyclisation then proceeds via the 1,3-elimination of bromine atoms and leads to a 45–50% yield of chlorocyclopropane. The presence of a chlorine atom in the γ-position relative to the geminal group sharply reduces the yield of the halogenocyclopropane. Thus in the case of 1,1-dibromo-3-chloropropane the yield of bromocyclopropane was 3–5% and the main product proved to be 1,6-dichlorohex-3-ene (40%).

Thus the 1,3-dehalogenation of *gem*-polyhalogeno-compounds with participation of bromine is also much easier than the reaction with participation of chlorine.

2. Reductive Cyclisation of Polychloro-derivatives

The ready availability of polychloroalkanes of the type of $CCl_3CH_2CClR^1R^2$ or $RCCl_2CClR^1R^2$, obtained by the addition of CCl_4 or $RCCl_3$ to the $>C=C<$ bond[67,68], makes it attractive to develop on their basis a method of synthesising compounds of the cyclopropane series. The study of chemical reactions of such polychloroalkanes suggested a new approach to the synthesis of cyclopropane and its substituted derivatives by the reductive cyclisation of the above compounds by zinc in boiling ethanol in a stream of HCl.[69]

In the present review reductive cyclisation is a term given to the process involving 1,3-dechlorination with formation of a new carbon–carbon bond (closure of a three-membered ring) and hydrogenolysis of one or two C–Cl bonds [mechanisms (2) and (3)]. It is noteworthy that the 1,3-elimination of two chlorine atoms from aliphatic compounds of the type of $RR^1CClCH_2CClR^2R^3$ with formation of the corresponding cyclopropane derivative is also sometimes referred to as reductive cyclisation[54] or reductive 1,3-elimination[5]. In the present review we shall refer to the reaction via mechanism (1) as 1,3-dechlorination in order to demonstrate its difference from reactions (2) and (3). Together with the above processes, hydrogenolysis, which does not lead to cyclopropane derivatives [reaction (4)], is also possible:

$$RCCl_2CH_2CClR^1R^2 \rightarrow \text{Cl, R, } R^1, R^2\text{-substituted cyclopropane}\ , \quad (1)$$

$$RCCl_2CH_2CClR^1R^2 \rightarrow \text{H, R, } R^1, R^2\text{-substituted cyclopropane}\ , \quad (2)$$

$$CCl_3CH_2CClR^1R^2 \rightarrow \text{H, H, } R^1, R^2\text{-substituted cyclopropane}\ , \quad (3)$$

$$RCCl_2CH_2CClR^1R^2 \rightarrow RCH_2CH_2CClR^1R^2 + RCH_2CH_2CHR^1R^2\ . \quad (4)$$

3. The Influence of the Nature of the Hydrogen Donor on the Yield of Cyclopropanes in the Reductive Cyclisation of Polychloroalkanes

The influence of various hydrogen donors on the yields of substituted cyclopropanes has been studied in relation to the compounds $(ClCH_2CH_2)_2CCl_2$ and $CH_3CCl_2CH_2CHClCH_3$ [70] (Table 2). In order to obtain comparable results, all the experiments, whose results are presented in Table 2, were performed up to ~100% conversion of the initial polychloroalkanes by heating the reaction mixture for 1–3 h.

Table 2. The yield of cyclopropanes in the reductive cyclisation of polychloroalkanes with zinc in various media[70].

Initial compound	Cyclopropane	Solvent				
		C_2H_5OH in stream of HCl	C_2H_5OH	CH_3CO_2H	$(CH_3)_2NCHO$	$[(CH_3)_2N]_3PO$
$(ClCH_2CH_2)_2CCl_2$	$\triangleright\!-CH_2CH_2Cl$	91	91	61*	53	70
$CH_3CCl_2CH_2CHClCH_3$	H_3C, CH_3 (*cis*:*trans*)	78 (7:1)	57 (6:1)	31 (4:1)	48 (10:1)	— —

*1,5-Dichloropentane (16%) was also obtained.

Table 2 shows that the best results have been obtained in experiments performed in boiling ethanol in a stream of HCl. Subsequently these conditions were used in the synthesis of a wide variety of cyclopropanes by the reductive cyclisation of polychloro-derivatives.

4. The Synthesis of Cyclopropane and Monosubstituted Cyclopropanes

Compounds having the structures CCl_3CH_2CHClR or $RCCl_2CH_2CH_2Cl$, containing the *gem*-polyhalogeno-group, readily react with zinc via one of the following mechanisms

$$RCCl_2CH_2CH_2Cl \xrightarrow[C_2H_5OH]{Zn} \triangleright\!\!-R \quad , \qquad (5)$$
$$R=(CH_2)_3\,Cl,\ (CH_2)_4\,Cl$$

$$CCl_3CH_2CHClR^1 \xrightarrow[C_2H_5OH]{Zn} \triangleright\!\!-R^1 \quad ; \qquad (6)$$
$$R^1=H,\ Alk.$$

The initial compound for the synthesis of cyclopropane is 1,1,1,3-tetrachloropropane [mechanism (6), $R^1 = H$], which can be readily obtained by the radical addition of CCl_4 to ethylene[67].

Reactions (5) and (6) involve both the *gem*-dichloromethylene and the *gem*-trichloromethyl groups. In both cases monosubstituted cyclopropanes are formed in high yields (Table 3). Under the chosen conditions, the formation of chlorocyclopropanes is not observed. Chloroalkanes [hydrogenolysis via mechanism (4)] have been obtained among the side products. Thus propyl chloride[71], 1,1,3-trichlorohexane[72], and 1,5-dichloropentane[69] have been isolated in low yields.

Table 3. The yields of cyclopropane and monosubstituted cyclopropanes* having the general formula $\triangleright\!\!-R$.

Initial compound	Yield, %	R	References
$CCl_3CH_2CH_2Cl$	75	H	[71]
$CCl_3CH_2CHClC_3H_7$	81	C_3H_7	[72]
$CCl_3CH_2CHClC_8H_{17}$	87	C_8H_{17}	[72]
$CCl_2(CH_2CH_2Cl)_2$	91	$(CH_2)_2Cl$	[69]
$ClCH_2CH_2CCl_2(CH_2)_4Cl$	86	$(CH_2)_4Cl$	[73]

*The reactions were performed in boiling ethanol with gaseous HCl passed for 1–3 h. The reactant ratio was polychloroalkane : zinc = 1 : 4.

5. The Synthesis of Monosubstituted Cyclopropanes with the Cyano- or Ester Group in the Aliphatic Chain

Polychloro-derivatives of the type $ClCH_2CH_2CCl_2CH_2.CClR^1X$ ($R^1 = H$ or CH_3; $X = CO_2CH_3$ or CN), containing a functional group in the α-position relative to the C–Cl bond, exhibit certain characteristic features in the reductive cyclisation reactions.

Table 4. The yields of monosubstituted cyclopropanes with functional groups in the side chain having the general formula $\triangleright\!\!-CH_2CHXR^1$ [74]*.

№	Initial compound	Yield, %	R^1	X
1	$ClCH_2CH_2CCl_2CH_2CHClCO_2CH_3$	67	H	CO_2CH_3
2	$ClCH_2CH_2CCl_2CH_2CCl(CH_3)CO_2CH_3$	63	CH_3	CO_2CH_3
3	$ClCH_2CH_2CCl_2CH_2CHClCN$	69	H	CN

*For the reaction conditions, see the footnote to Table 3.

The reaction proceeds selectively with respect to the $ClCH_2CH_2CCl_2$-fragment, while the chlorine atom in the α-position relative to the electron-accepting group (CN, CO_2R) is replaced by hydrogen and is not involved in the reductive cyclisation:

$$ClCH_2CH_2CCl_2CH_2CClXR^1 \xrightarrow[EtOH\ or\ MeOH]{Zn} \triangleright\!\!-CH_2CHXR^1 \ ;$$
$$R^1=H,\ CH_3;\ X=CN,\ CO_2CH_3 \ .$$

As a result, high yields of monosubstituted cyclopropanes with electron-accepting groups in the side chain are produced (Table 4).

Among the side reactions, mention may be made of the hydrogenolysis of the $\gtrdot CCl_2$ group. For example, $Cl(CH_2)_5CO_2CH_3$ has been obtained in a low yield from $ClCH_2CH_2CCl_2CH_2CHClCO_2CH_3$. The hydrolysis of the cyano-group on cyclisation of $ClCH_2CH_2CCl_2CH_2CHClCN$ to the acid with subsequent esterification, leading to cyclo-$C_3H_5CH_2CH_2CO_2C_2H_5$ with a low yield, has also been noted.

6. The Syntheses of Di-, Tri-, and Tetra-substituted Alkyl-, Chloroalkyl-, Phenyl-, and Chlorophenyl-cyclopropanes

If the substituents R, R^1 and R^2 in the initial polychloroalkanes $CCl_3CH_2CClR^1R^2$ or $RCCl_2CH_2CClR^1R^2$ are varied, it is possible to obtain disubstituted cyclopropanes (vicinal or geminal) as a result of reductive cyclisation and also tri- and tetra-substituted cyclopropanes by one of the following mechanisms:

$$CCl_3CH_2CClR^1R^2 \xrightarrow[C_2H_5OH]{Zn} \triangleright\!\!-R^1 + \triangleright\!\!-R^1 + \triangleright\!\!-R^1 \quad ; \qquad (7)$$
$$R^2 \qquad Cl\ R^2 \qquad Cl\ R^2$$

$$RCCl_2CH_2CClR^1R^2 \xrightarrow[C_2H_5OH]{Zn} \triangleright\!\!-R^1 + \triangleright\!\!-R^1 \quad ; \qquad (8)$$
$$R \quad R^2 \qquad R \quad R^2$$

$R=CH_3;\ R^1=H,\ CH_3;\ R^2=CH_3,\ C_6H_5.$

Examples of these reactions are given in Table 5.

Table 5. The yields and configurations of di-, tri-, and tetra-substituted cyclopropanes* .

№	Initial compound	Substituted cyclopropanes	Configuration*	Yield, %	Refs.
1	$CH_3CCl_2CH_2CHClCH_3$	H_3C—$\triangleright$—CH_3	Z	68	[75]
			E	10	
2	$CH_3CCl_2CH_2CHClC_6H_5$	H_3C—$\triangleright$—C_6H_5	Z	3	
			E	3	
		H_3C—$\triangleright$(Cl)—C_6H_5	Z	17	[71]
			E	39	
3	$CCl_3CH_2CHClC_6H_5$	$\triangleright$—C_6H_5	—	38	
			Z	4	[71]
		Cl—$\triangleright$—C_6H_5	E	11	
		Cl—$\triangleright$(Cl)—C_6H_5	—	11	
4	$CCl_3CH_2CCl(CH_3)_2$	$\triangleright$(CH_3)(CH_3)	—	44	[76]
5	$CH_3CCl_2CH_2CCl(CH_3)_2$	H_3C—$\triangleright$(CH_3)—CH_3	—	46	[76]
		H_3C—$\triangleright$(CH_3)(Cl)—CH_3	—	13	

*For the reaction conditions, see the footnote to Table 3.
**The geometrical isomers are designated in terms of the nomenclature of Blackwood et al.[77], based on the concepts of the *E*- and *Z*-forms.

Evidently the chlorine atom at a secondary carbon atom is readily involved in the reductive cyclisation. We may note that the synthesis of vicinal dialkylcyclopropanes results in the preferential formation of the *cis*-isomer (Table 5, No.1). The secondary benzylic chlorine atom can also be involved in the reaction. A characteristic feature of the reductive cyclisation of compounds with a benzylic chlorine atom is the formation of chlorocyclopropanes (Table 5, Nos.2 and 3), which indicates the influence of the bulk of the substituent at a secondary carbon atom linked to a single chlorine atom on the hydrogenolysis of the C–Cl bond in the CCl_2 or CCl_3 group on cyclisation of compounds of the type $XCCl_2CH_2.CHClC_6H_5$ (X = Cl or alkyl). For examples under discussion, the formation of n-propyl- or n-butyl-benzenes (in low yields) as side products has been noted.

The chlorine atom at a tertiary carbon atom is also involved in the reductive cyclisation. The resulting *gem*-dimethylcyclopropane is insufficiently stable under the experimental conditions (Table 5, No.4) and isomerises with ring opening. This entails the formation of 2-methylbut-1-ene and 3-methylbut-1-ene with an overall yield of 36%. Chlorocyclopropanes have been obtained not only by the reductive cyclisation with involvement of a benzylic chlorine atom but also in the case where the chlorine atom is linked to a tertiary carbon atom (Table 5, No.5). This shows that the number of substituents at the carbon atom linked to the chlorine atom influences the hydrogenolysis of the C–Cl bond in the dichloromethylene group. Evidently in the instances indicated above such hydrogenolysis is hindered, which leads to the formation of chlorocyclopropanes.

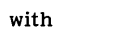
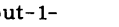
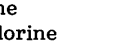
Consideration of the results of the reaction of 1,1,1,3-tetrachloro-3-phenylpropane with zinc shows that the overall yield of substituted cyclopropanes is 64% and that the products represent as it were all the stages in the reductive cyclisation: 1,1-dichloro-2-phenylcyclopropane, which is the 1,3-dechlorination product, and 1-chloro-2-phenyl- and 1-phenyl-cyclopropanes, which are the products of the successive substitution of chlorine by hydrogen. However, the chlorocyclopropanes formed are not intermediates whose hydrogenolysis leads to the formation of their hydrocarbon analogues, because it is known that chlorocyclopropanes are inert to reduction by zinc in alcohol[78]. Furthermore, special experiments have established that the interaction of 1,1-dichloro-2-phenylcyclopropane or 1-chloro-1-methyl-2-phenylcyclopropane with zinc under the conditions of reductive cyclisation leads to the formation of reduction products—1-chloro-2-phenylcyclopropane or 1-methyl-2-phenylcyclopropane—only in insignificant yields (2–7%).[70]

At the end of this discussion of the reductive cyclisation of polychloroalkanes with the $XCCl_2CH_2CCl<$ (X = Cl or alkyl) group, one may conclude that, in those cases where a single chlorine atom is linked to a primary or secondary carbon atom, the reaction proceeds smoothly and leads to the formation of mono- or di-substituted cyclopropanes in high yields. In those cases were a benzylic chlorine atom or a chlorine atom attached to a tertiary carbon atom is involved in the reaction, there is a possibility of the formation of a mixture of cyclopropane derivatives containing chlorocyclopropanes.

7. Competing Pathways in the Reductive Cyclisation of Polychloroalkanes with Several Chlorine-containing Groups

If there are several different chlorine-containing groups in the polychloroalkane molecule, the mode of reaction of this compound with zinc depends on the relative positions of the chlorine atoms. The study of the competing processes made it possible to establish the limits of the applicability of the given method of synthesis of cyclopropane compounds and to obtain data from which the reaction mechanism can be inferred. Certain examples of such reactions are given in Table 6.

Table 6. The reactions of monofunctional polychloroalkanes*.

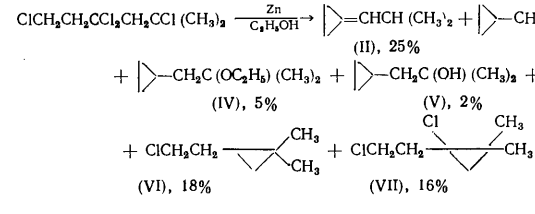
№	Initial compound	Products	Yield, %	References
1	$ClCH_2CH_2CCl_2CH_2CHClCH_3$		38	[75]
		 (*cis*)	32	
2	$ClCH_2CH_2CCl_2CH_2CHCl_2$		60 (72)**	[75]
			11 (2)	
3	$ClCH_2CH_2CCl_2CH_2CHClCH_2Cl$		60	[74]
4	$(ClCH_2CH_2CCl_2)_2$	$(ClCH_2CH_2CCl{=})_2$	92	[74]

*For the reaction conditions, see the footnote to Table 3.

**The yields of products obtained under the following reaction conditions are indicated in brackets: 25 °C, solvent—DMF.

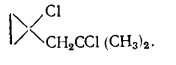
***The 1,2-dechlorination products, namely 6-chlorohex-1-ene and 3-cyclopropylpropene, were not detected.

Table 6 shows that, if the reductive cyclisation can proceed with participation of the chlorine atom at a primary or secondary carbon atom, then both possible pathways operate to approximately equal extents and a mixture of mono- and di-substituted cyclopropanes is obtained (Table 6, No.1). On the other hand, if there is a possibility of competition between 1,3-dechlorination with participation of the chlorine atom at a primary or tertiary carbon atom, the reaction is more complex[76] and a number of products are formed:



Compounds (II)–(V) are then produced as a result of reductive cyclisation with participation of the chlorine atom at a primary carbon atom, while compounds (VI) and (VII) result from 1,3-dechlorination involving the chlorine atom at a tertiary carbon atom. The overall yields of compounds formed on cyclisation via both competing pathways amounted to 41 and 34% respectively. This shows that the two processes take place to approximately equal extents. It is noteworthy that 1,3-dechlorination with participation of a single chlorine atom at a tertiary carbon atom leads to the formation of chlorocyclopropane (VII). Cyclopropane (II), having an exocyclic double bond, has been obtained with an

appreciable yield. Its formation is due to the 1,3-dechlorination of the $ClCH_2CH_2CCl_2$ fragment and subsequent transformations of the intermediate

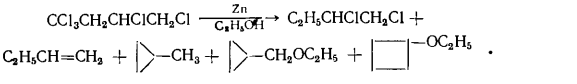


The $CHCl_2$ group in 1,1,3,3,5-pentachloropentane is involved in reductive cyclisation with much more difficulty than the $ClCH_2$ group (Table 6, No.2). Indeed, 60% of the reaction products were obtained by the cyclisation of the $ClCH_2CH_2CCl_2$ fragment. The formation of $CHCl_2(CH_2)_4Cl$ (5%) as a result of the hydrogenolysis of the CCl_2 group as well as the formation of a mixture of unsaturated chloroalkenes and the ethers $CH_2 = C(CH_2CH_2Cl)CH_2OC_2H_5$ and $CH_2 = C(CH_3)CH_2CH_2Cl$ (overall yield 12%) as a result of isomerisation with ring opening have also been noted. The formation of products of hydrogenolysis and isomerisation with ring opening does not occur if the reaction is carried out in DMF. The reductive cyclisation of the $CHCl_2CH_2CCl_2$ fragment is examined in greater detail below (see Section IV).

Results important for the understanding of the mechanism of the reductive cyclisation have been obtained in a study of polychloroalkanes which can undergo either 1,3- or 1,2-dechlorination. These compounds include $XCCl_2CH_2.CHClCH_2Cl$ (X = Cl, CH_3, or $ClCH_2CH_2$) and $(ClCH_2CH_2.CCl_2)_2$.

Table 6 shows that, when there is a possibility of the competitive 1,3-dechlorination of the $ClCH_2CH_2CCl_2$ group and the 1,2-dechlorination of single chlorine atoms, then the main reaction pathway is 1,3-dechlorination (Table 6, No.3). On the other hand, if 1,3-dechlorination of the same group or 1,2-dechlorination of vicinal dichloromethylene groups is possible, the only reaction pathway becomes 1,2-dechlorination of the $-CCl_2CCl_2-$group (Table 6, No.4). These results indicate unambiguously that the reaction begins with attack by the zinc atom on the $>CCl_2$ group.

Further confirmation of this has been obtained in the study of the interaction of polychloroalkanes of the type $XCCl_2.CH_2CHClCH_2Cl$ (X = Cl or CH_3) with zinc[71,74]. In relation to $CCl_3CH_2CHClCH_2Cl$, the reaction proceeds via the mechanism

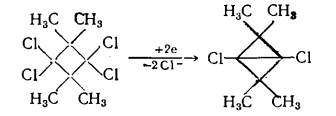


Similar results have been obtained in the study of the interaction of 2,2,4,5-tetrachloropentane with zinc in alcohol. The main products of these reactions are 1,2-dichloroalkanes and alk-1-enes—formed with an overall yield of 50–60% as a result of the hydrogenolysis of the CCl_3 or $>CCl_2$ groups. Cyclisation of the $CCl_2CH_2CHClCH_2Cl$ fragment containing the CH_2Cl group in the α-position relative to the single Cl atom is much more difficult (see also Table 6, No.3). The overall yield of cyclic products is only 6–9%.

Thus in these cases too the reaction begins with attack by zinc on the $>CCl_2$ group. The hydrogenolysis of the *gem*-polychloroalkyl group in the absence of the chlorine atom in the γ-position relative to this group becomes the only reaction pathway. Indeed, under the conditions of reductive cyclisation, mainly 1,1,5-trichloropentane is obtained from 1,1,1,5-tetrachloropentane[72].

IV. 1,3-DECHLORINATION OF COMPOUNDS WITH THE GROUPS $-CCl_2CH_2CCl_2-$ or $CCl_3CH_2CCl_2-$

1,3-Dechlorination of compounds with the $-CCl_2CH_2CCl_2-$group is known to occur in a few isolated examples. Thus, 1,1,3,3-tetrachloro-2,2,4,4-tetramethylcyclobutane has been reduced electrochemically at a mercury cathode in DMF:[79]

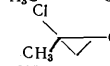


The reaction proceeds with formation of 1,3-dichlorotetramethylbicyclobutane.

Polychloroalkanes with two $>CCl_2$ groups in the 1,3-positions (of the type of $RCCl_2CH_2CCl_2CH_3$) can be readily achieved by adding $RCCl_3$ to 2-chloropropene[80,81]. It might be supposed that 1,2-disubstituted cyclopropenes would be formed from these compounds under the conditions of reductive cyclisation. However, it was found that the results of the reaction depend greatly on the structure of the geminal groups (CCl_3, CCl_2, or $CHCl_2$) and on the reaction conditions.

Table 7 presents data obtained for various polychloroalkanes when the latter are refluxed with zinc in ethanol. It was shown that the reaction proceeds in a complex manner with formation of a mixture of saturated and unsaturated cyclic and aliphatic compounds. Cyclopropenes have been obtained only from $CHCl_2CH_2CCl_2CH_3$; the formation of chlorocyclopropanes has also been noted[82]. The presence of branched unsaturated products in the mixtures can be explained by the fact that chlorocyclopropanes are apparently unstable under the reaction conditions and isomerise with ring opening. In all three examples in Table 7 products of the hydrogenolysis of the $>CCl_2$ group are formed.

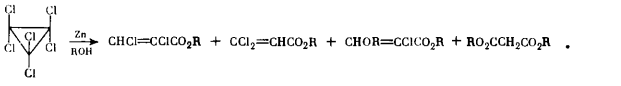
Table 7. The yields of the products of reductive cyclisation with participation of the $-CCl_2CH_2CCl_2-$group in C_2H_5OH (78 °C, 3 h).

Initial compound	Cyclic compounds	Yield, %	Aliphatic compounds	Yield, %	Refs.
$CHCl_2CH_2CCl_2CH_3$		30	$CHCl_2CH_2CH_2CH_3$	12	
		4	$CH_2=C(CH_3)CH_2OC_2H_5$	19	[75]
		10	$CH_2=C(CH_3)_2$	9	
$CH_3CCl_2CH_2CCl_2CH_3$		4	$CH_2=C(CH_3)CH(CH_3)OC_2H_5$	30	
			$CH_2CH=C(CH_3)CH_2OC_2H_5$	3	
		9	$CH_3(CH_2)_3CH_3$	1	[82]
		4	$CH_3CH=CHC_2H_5$ / $CH_2=C(CH_3)C_2H_5$	11	
			$CHCl_2CH_2CH_2Cl$	38	
			$CHCl_2CH_2CH_2OC_3H_7$	21	[74]
$CHCl_2CH_2CHCl_2$*	—	—	$CHCl_2CH_2CH_3$	20	
			$Cl(CH_2)_3Cl$	4	

*The reaction was carried out in $n\text{-}C_3H_7OH$ at 100 °C for 3 h.

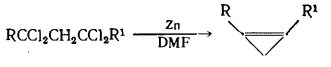
$CHCl_2CH_2CHCl$ does not react with zinc in boiling ethanol. On the other hand, in boiling propanol the hydrogenolysis of the $CHCl_2$ group, and not 1,3-dechlorination, takes place with subsequent alkoxylation.

The formation of a complex mixture of products has been observed in a study of the action of zinc in ethanol on hexachlorocyclopropane[83]. Instead of the expected 1,2,3,3-tetrachlorocyclopropene, a mixture of unsaturated esters was obtained, the esters being formed, according to the authors[83], as a result of isomerisation with opening of the cyclopropane ring:



1. The Synthesis of Substituted Cyclopropenes

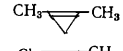
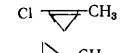
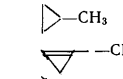
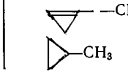
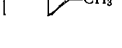
Reduction of the reaction temperature and especially the use of a different solvent (replacement of C_2H_5OH by DMF) enabled Kamyshova et al.[84] to propose a new method of synthesis of substituted cyclopropenes. The reaction proceeds via the mechanism



The availability of compounds of the type $RCCl_2CH_2CCl_2CH_3$ noted above leads to the possibility of synthesising the corresponding 1,2-disubstituted cyclopropenes; examples of such reactions are given in Table 8. Evidently, when R,R^1 = alkyl, the reaction leads to the formation of 1,2-dialkylcyclopropenes in high yields (Table 8, Nos.1 and 2). In those cases where the molecule contains only one CCl_2 group and the second geminal group is either CCl_3 (R = Cl, Table 8, No.3) or $CHCl_2$ (R = H, Table 8, No.4), the reaction is more complex and leads to a mixture of monosubstituted cyclopropanes and cyclopropenes.

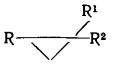
The synthesis of cyclopropenes from polychloroalkanes with the $-CCl_2CH_2CCl_2$-group by the action of zinc in DMF is extremely promising, since cyclopropenes are formed under mild conditions and in high yields.

Table 8. The synthesis of cyclopropenes by the dechlorination of compounds of the type $RCCl_2CH_2CCl_2CH_3$ with zinc in DMF at 25 °C.

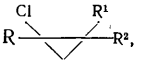
№	Initial compound	Cyclic compounds	Yield, %	Refs.
1	$CH_3CH_2CCl_2CH_2CCl_2CH_3$		77	[85]
2	$CH_3CCl_2CH_2CCl_2CH_3$		73	[84]
3	$CCl_3CH_2CCl_2CH_3$		29	[85]
			4	
4	$CHCl_2CH_2CCl_2CH_3$		56	[85]
			8	

V. THE PROBLEM OF THE MECHANISM OF THE REDUCTIVE CYCLISATION OF POLYCHLOROALKANES WITH FORMATION OF THREE-CARBON RINGS

The mechanism of the dehalogenation of 1,3-dihalogenoalkanes to compounds of the cyclopropane series by metals or salts of metals in the lowest valence state has been the subject of a series of studies (see, for example, Refs.54, 58, 66, 86, 87). It was found that the process is complex and consists of two or three stages[86,87]. In almost all the studies the possibility of the intermediate formation of a γ-halogeno-substituted organometallic compound was considered. For example, the cyclisation of 1,3-dihalogenopropane under the influence of the $Cr(ClO_4)_2$–ethylenediamine complex entails, according to Kochi and Singleton[54], the intermediate formation of $HalCH_2CH_2CH_2Cr^{II}en$, where en = ethylenediamine. The cyclisation of 2-benzyl-1,3-di-iodo-2-methylpropane by $LiAlH_4$ in ether is also believed[58] to involve the intermediate formation of the organoaluminium compound $PhCH_2C(CH_3).(CH_2I)CH_2LiAlH_3$. It is believed[66] that 1,1,3-dehalogenation of 1,1,3-trihalogenoalkanes with methyl-lithium proceeds via the intermediate formation of organolithium compounds of the type $RCHBrCH_2CHHalLi$. As regards the reductive cyclisation of compounds of the type $RCCl_2CH_2.CClR^1R^2$ by the action of zinc, which involves both 1,3-dechlorination and the hydrogenolysis of the C–Cl bond, one may claim that the hydrogenolysis of the CCl_2 group with formation of the fragment $\rangle CClCH_2CCl\langle$ is not the first reaction stage, since this fragment is dechlorinated with much more difficulty (see Section II), than the $-CCl_2CH_2CCl\langle$ group. One may also claim that the formation of the cyclopropanes



does not proceed via the intermediate chlorocyclopropanes

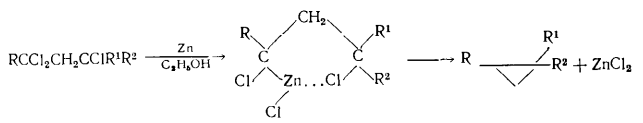


because, as already stated above, under the conditions of reductive cyclisation the hydrogenolysis of the chlorine atom linked to the ring proceeds to an insignificant extent (see Section III).

One may quote much evidence in support of the fact that reductive cyclisation with participation of *gem*-polyhalogeno-groups begins with attack by the zinc atom on such a group (CCl_2 or CCl_3). Thus there are two vicinal CCl_2 groups and the $ClCH_2$ group in the compound $(ClCH_2CH_2CCl_2)_2$; the reaction proceeds solely with the participation of the $-CCl_2CCl_2$-group, while the CH_2Cl group is not involved at all. On the other hand, the 1,3-dechlorination of the $ClCH_2CH_2CCl_2$ fragment in the $ClCH_2CH_2CCl_2CH_2CHClCH_2Cl$ molecule takes place much more readily than the 1,2-dechlorination of single chlorine atoms. The main reaction pathway for compounds of the type $XCCl_2CH_2CHClCH_2Cl$ (X = Cl or alkyl) is the hydrogenolysis of the $XCCl_2$ group. It has also been shown that $AlkCCl_2CH_2CHCl_2$ is 1,3-dechlorinated, whereas $CHCl_2CH_2CHCl_2$ is not involved in cyclisation. All these findings indicate the necessity for the presence in the molecule of the dichloromethylene or the trichloromethyl group for the reaction under consideration to occur. Finally reductive cyclisation proceeds just as readily when it involves a single Cl atom linked to a primary, secondary, or tertiary carbon atom.

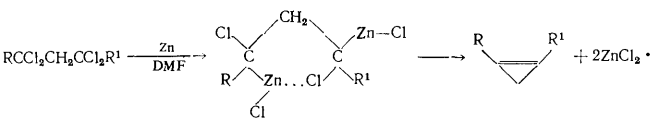
By analogy with the examples of the 1,3-dehalogenation of dihalogenoalkanes by metals with the intermediate formation of organometallic compounds, which were examined above, one can postulate that the reductive cyclisation of polychloroalkanes of the type $RCCl_2CH_2CClR^1R^2$ also proceeds via the intermediate formation of an organozinc compound. This hypothesis makes it possible to account for the ready

hydrogenolysis of the C–Cl bond in the α-position relative to the C–Zn bond:

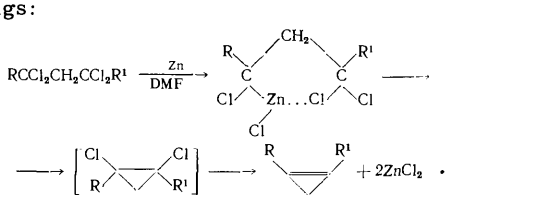


This hypothesis is also confirmed by the preferential formation of *cis*-1,2-disubstituted cyclopropanes mentioned above. The stereoselectivity of the process shows that an organozinc compound is formed as an intermediate in a specific conformation ensuring the coordination of zinc to γ-chlorine. The elimination of $ZnCl_2$ leads to the closure of the three-carbon ring.

1,2-Disubstituted cyclopropenes are apparently formed by a similar mechanism:



An alternative reaction involves the initial 1,3-dechlorination to 1,2-dialkyl-1,2-dichlorocyclopropane followed by 1,2-dechlorination of the vicinal chlorine atoms of the three-carbon rings:



Thus compounds with the groups CCl_3CH_2CCl <, $-CCl_2CH_2CCl$ <, or $-CCl_2CH_2CCl_2-$ can find extensive applications in the synthesis on their basis of a wide variety of three-carbon rings via dechlorination or reductive cyclisation reactions.

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Derivatives of Carbohydrates with Carbamide Fragments

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A systematic account is given of the results of experimental studies on the synthesis, structures, and properties of carbohydrate-containing derivatives of urea and its analogues—thiourea, selenourea, and iminourea (guanidine). The possibility of using them in the preparative chemistry of carbohydrates and in certain branches of the national economy is demonstrated. The prospects for the development of the chemistry of sugars with ureido-groups are outlined.

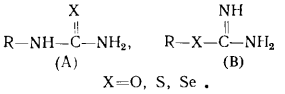
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I. INTRODUCTION

The products of the substitution of the hydroxy-groups of the carbohydrate chain, including the glycosidic hydroxyl $C_{(1)}$–OH by the residues of derivatives of urea and its analogues—thiourea, selenourea, and guanidine (iminourea)—must be included among ureidosugars, which form part of the large class of aminosugars and *N*-glycosylamines (*N*-glycosides).[1-4] A series of structural and chemical features make it possible to combine these compounds into a separate group among nitrogen-containing sugar derivatives. Among these features, one should include in the first place the polyfunctional nature of the carbamide fragments, manifested particularly by the effects involving neighbouring functional groups of the sugars. The presence of the carbonyl group in the immediate vicinity of the amino-group reduces markedly the basicity (pK_a) of the amino-group and hence the reactivity of the carbamide fragment in acid-catalysed nucleophilic addition and substitution reactions. In this respect the *N*-glycosidic linkage in *N*-glycosyl derivatives of carbamides approaches in its properties the glycosidic linkages in nucleosides. The fact that both the amino-group (A) and the oxygen, sulphur, and selenium atoms (B) can participate in the formation of a bond with the carbohydrate residue R must be regarded as one of the characteristic features of ureidosugars, the stability of derivatives with the iso-structure (B) increasing with increase of the nucleophilicity of the atom X. Stable iso-structures of carbohydrate derivatives of urea are unknown.



X=O, S, Se.

In terms of certain structural and chemical features, ureidosugars resemble carbamic acid esters (carbanilates) and amides derived from sugars as well as *N*-acylation products. The preparative value of these derivatives in carbohydrate chemistry has been discussed in a number of studies[1-5] and they are not considered in the present review.

Different aspects of the technical employment of ureidosugars are limited mainly to *N*-glycosylureas, which have been used, for example, to obtain non-shrinking and crease-resistant cotton fabric[6], in compositions designed to increase the strength of paper[7], as detergents with improved disinfecting properties[8,9], and as feed preparations with a high content of *N*-glycosylurea to make good the protein nitrogen deficiency in the diet of animals[10,11]. A significantly more important trend towards their application in pharmacology, medicine, the health service, bio-organic chemistry, and molecular biology has arisen recently. The likelihood of the development of research into the chemistry of ureidosugars is associated primarily with the problem of the synthesis of carbohydrate-containing physiologically active substances with a low toxicity, a high solubility in water, and with selective action on the living organism.

As a preparation for medical purposes, urea has extremely modest possibilities[12]. Urea derivatives, the various pharmacological properties of which can be illustrated by examples of their utilisation as soporific, narcotic, antipyretic, analgesic, and anticonvulsant agents and in the treatment of diabetes, glycaemia, and in helminthiasis, are of significantly greater interest in this sense[12-14]. The fact that the carbamide residue is extremely common in nature and enters into the structures of biologically important substances of the pyrimidine series also merits special attention. Nitroso-derivatives of urea, guanidine, and biuret have acquired great practical importance for the treatment of malignant neoplasts[15-19]. An exceptionally high mutagenic activity and the ability to overcome the haematoencephalic barrier must be included among the characteristic features of *N*-nitrosoalkylureas.

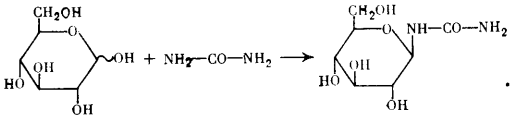
Bearing in mind the above considerations, it is to be expected that the development of experimental and theoretical studies in the field of carbohydrate-containing derivatives of urea and its analogues will lead to the discovery of ways of synthesising new effective medicinal drugs and intermediates for their preparation.

II. METHODS OF SYNTHESIS OF UREIDOSUGARS

Two main approaches are used in the synthesis of ureidosugars: direct interaction of carbohydrates with carbamides and their analogues under the conditions of acid catalysis and the formation of carbamide groups in the carbohydrate molecule on the basis of known reactions leading to the formation of derivatives of urea, thiourea, selenourea, and guanidine. The first pathway is suitable for the synthesis of derivatives involving the glycosidic centre. Among the methods of the second type, the iso(thio)cyanate

method has become most widely used, permitting the introduction of the carbamide residue into virtually any position in the carbohydrate ring.

The synthesis of *N*-glucosylurea (II) by the direct condensation of unsubstituted D-glucose (I) with urea in the presence of an inorganic acid as the catalyst was first achieved by Schoor[20]:

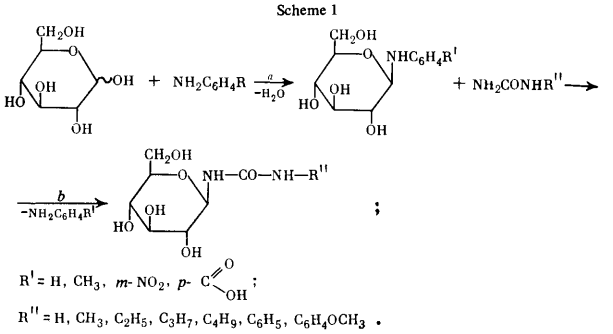


(I) (II)

The reaction was followed by measuring the optical rotation of the reaction solution. The crystalline product was obtained only after enzymatic cleavage of the unreacted D-glucose. Subsequently, the direct condensation method was improved somewhat[21-29] and extended to other mono- and di-saccharides, but no fundamental changes were introduced into the method of synthesis. Thus in the synthesis of *N*-β-D-glucopyranosylurea[21] a 1:1 mixture of glucose and urea is kept at 50 °C for seven days, evaporated, and the 1:2 adduct of glucosylurea and urea is crystallised. In order to isolate glucosylurea, the product is treated with boiling absolute ethanol for three days. In the synthesis of *N*-β-D-ribopyranosylurea[23] the reaction mixture is kept at 50 °C for ten days and the anomeric forms of the condensation product are isolated by preparative chromatography; the final yield does not exceed 15–20%.

A new, more effective method of synthesis of *N*-glycosylurea, using unprotected *N*-arylglycosides, has been discovered in recent years[30-32]. Kinetic studies have shown[2] that the replacement of the glycosidic hydroxyl by an *N*-arylaglycone increases the reactivity of $C_{(1)}$ in nucleophilic addition and substitution reactions as a result of which it is possible to facilitate the introduction of weakly basic aglycones under the conditions of acid catalysis. The set of reactions involving the $C_{(1)}$ atom in the synthesis of *N*-glycosylureas can be represented by the following scheme incorporating stages (*a*) and (*b*):

Scheme 1



R^{I} = H, CH_3, *m*-NO_2, *p*-$C(=O)OH$;

R^{II} = H, CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5, $C_6H_4OCH_3$.

In order to obtain *N*-glycosylureas by the *N*-transglycosylation reaction, it is sufficient to heat for a very short time (10–30 min) a mixture of urea and the *N*-arylglycosides with an aglycone of moderate basicity in the presence of small amounts of added inorganic acid until the mixture becomes completely homogenised. The initial *N*-glycoside is sometimes precipitated on crystallisation together with the required product, but it can be readily removed by washing the precipitate with hot ethanol. Subsequent recrystallisation of the product from aqueous alcoholic solutions leads to chromatographically homogeneous *N*-β-D-glycopyranosylurea.

Scheme 1 shows that the arylamine plays in essence the role of a nucleophilic catalyst of the direct condensation of the monosaccharide with urea derivatives. To simplify the preparative procedure, *N*-glycosylureas can therefore be synthesised without the preliminary preparation of the corresponding *N*-arylglycoside and catalytic amounts of the arylamine can be used.

In the synthesis of glycosylureas by the direct condensation of unprotected sugars with urea, *N*,*N'*-diglycosylureas are always formed, their relative content in the reaction mixture depending on the ratio of the concentrations of the initial components:

$$2\rangle HC_1{-}OH + NH_2{-}CO{-}NH_2 \rightarrow \rangle HC_1{-}NH{-}CO{-}NH{-}C_1H\langle + 2H_2O .$$

N-Alkylureas do not condense with sugars at the site where the alkyl group is substituted.

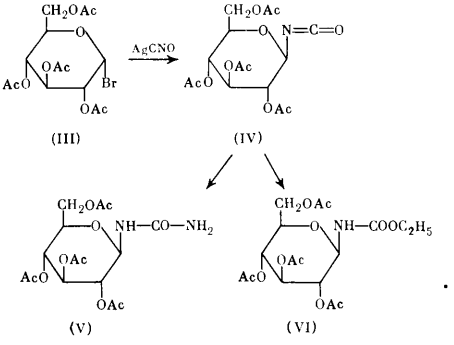
The *N*-triglycosylation method is nowadays the most promising for the synthesis of *N*-glycosylureas on a large scale. By altering the nature of the *N*-aglycone, it is possible to vary the rate of the substitution reaction and to synthesise anomeric forms at the kinetically controlled stages.

The isocyanate method, developed by Fischer[33] in 1914 and based on the interaction of acetyl-substituted glycosyl isocyanates with amines, proved to be effective in the synthesis of *N*-glycosylureas:

$$\rangle HC_1{-}N{=}C{=}O + NH_2R \rightarrow \rangle HC_1{-}NH{-}CO{-}NHR .$$

Thus, in the synthesis of *N*-β-D-glucopyranosylurea, treatment of tetra-*O*-acetyl-α-D-glycopyranosyl bromide (III) with silver cyanate in anhydrous xylene gives the glucosyl isocyanate (IV) which is converted into the final product (V) by teatment with an aqueous solution of ammonia. On the other hand, when compound (IV) is heated in an alcoholic solution, the glucosylurethane (VI) is formed (see the scheme below):

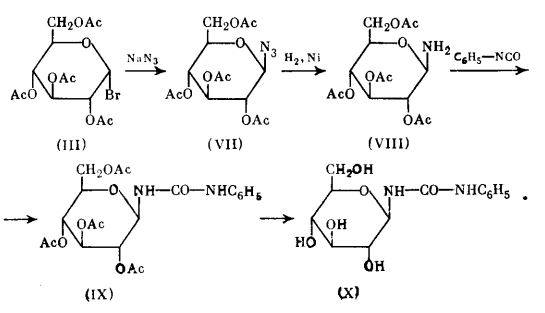
Scheme 2



(III) (IV) (V) (VI)

The carbamide residue can be formed at $C_{(1)}$ also by the reaction of *N*-glycosylamine with isocyanates, as shown for the formation of *N'*-phenyl-*N*-β-D-glucopyranosylurea (X) (see the scheme below):

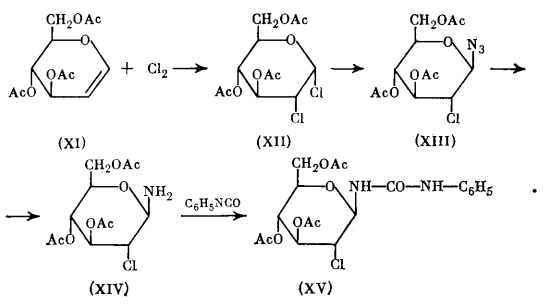
Scheme 3



(III) (VII) (VIII) (IX) (X)

The Fischer method has been improved[34-41] and its applicability in the synthesis of glycosylureas has been greatly extended. An an illustration, one may quote the synthesis of 2-chloro- and 2-bromo-derivatives of glycosylureas from acetylglycols[42]:

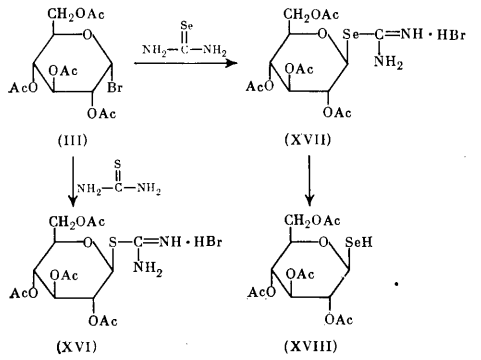
Scheme 4



Similarly sugar isothiocyanates with protected hydroxy-groups readily undergo addition reactions with amines and give rise to the corresponding *N*-glycosylthioureas.

The interaction of thiourea with acetylhalogeno-sugars leads to the formation of thioureido-sugars with the iso-structure. Thus treatment of acetobromoglucose (III) with thiourea results in the formation of tetra-*O*-acetyl-β-D-glucopyranosylisothiourea (XVI)—the so-called "isothiouronium salt":[48-51]

Scheme 5

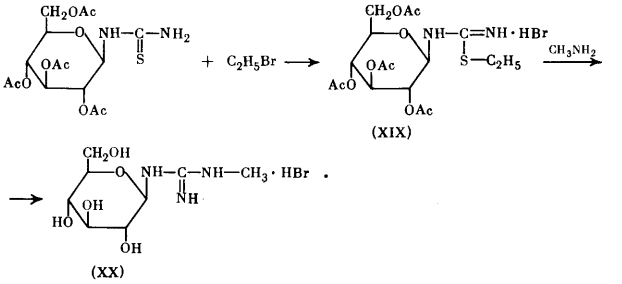


Derivatives of isothiourea are unstable and readily decompose under the influence of bases with formation of thioaldoses. A method of synthesis of alkylthioglycosides has been developed on this basis[52].

Selenourea behaves analogously[53-56]. On interaction with acetobromoglucose, it gives rise to tetra-*O*-acetyl-β-D-glucopyranosylisoselenourea (XVII), which decomposes on treatment with KOH solution to form the selenoglucoside (XVIII), which subsequently condenses to bis(tetra-*O*-acetyl-β-D-glucopyranosyl) diselenide.

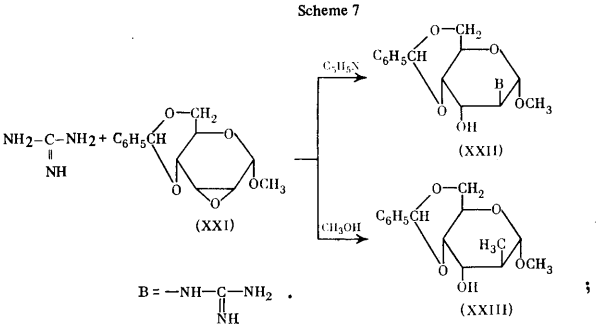
In contrast to urea and thiourea, guanidine does not undergo condensation reactions with unsubstituted sugars[4]. Guanidine-containing sugars can be conveniently obtained by the method involving the transformation of the thiourea fragment into a guanidine fragment by treatment with amines[57-59]. This procedure can be illustrated in relation to the synthesis of *N*-β-D-glucopyranosylguanidine (XX) from *S*-ethyl-substituted *N*-β-D-glucopyranosylthiourea (XIX) obtained by the reaction of *N*-β-D-glucopyranosylthiourea with ethyl bromide and subsequent treatment with methylamine[57,58]:

Scheme 6



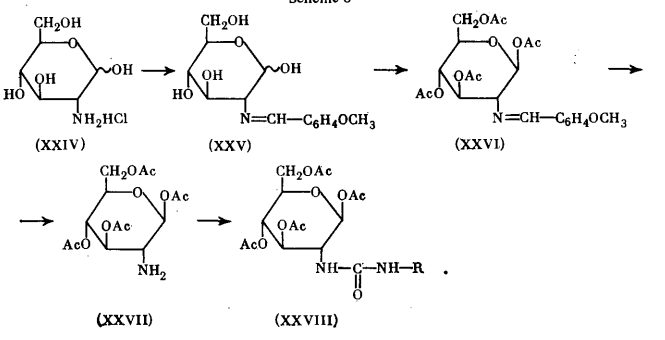
It has been possible[60-62] to introduce the guanidino-residue into the $C_{(2)}$ position by the direct treatment of 2,3-anhydro-4,6-*O*-benzylidene-α-D-methylallopyranoside (XXI) with guanidine, the mixture being subjected to prolonged heating in pyridine. When the treatment with guanidine was carried out in methanol, the methyl derivative (XXIII) was formed via the following scheme:

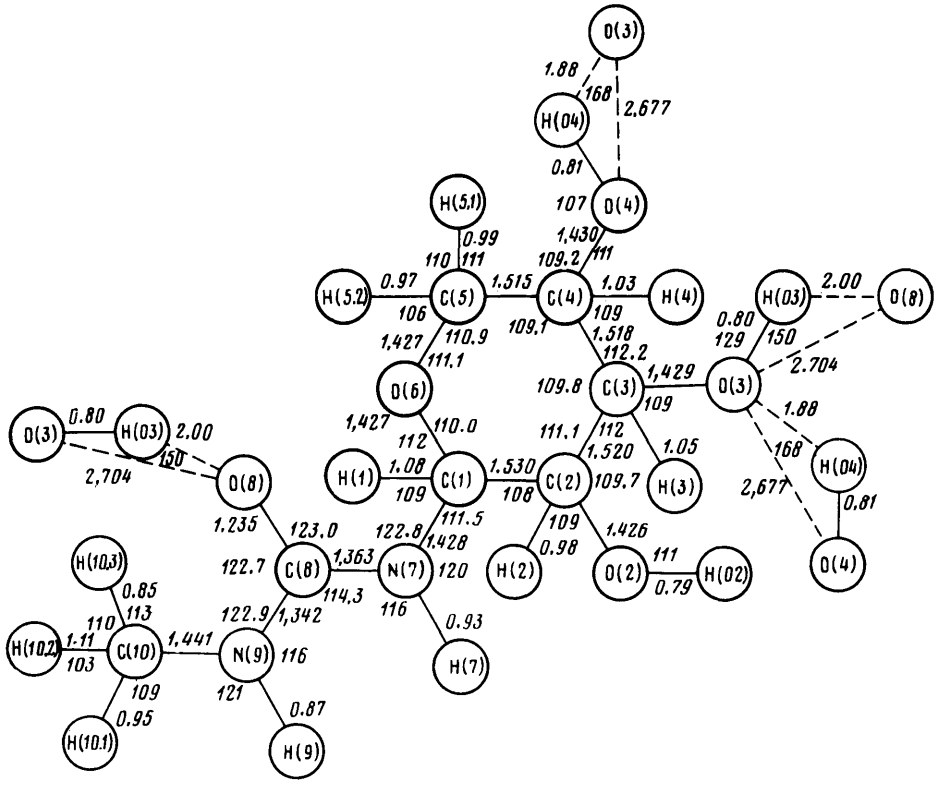
Scheme 7



The Fischer iso(thio)cyanate method, which is universal and preparatively simple, is mainly used to introduce carbamide or thiocarbamide fragments into positions in the carbohydrate ring other than the glycosidic centre at $C_{(1)}$. The applicability of this method of synthesis is determined by the practical availability of aminosugars with a specified position of the amino-group. The method of synthesis can be illustrated by the synthesis via Scheme 8 of *N*-substituted derivatives of 2-ureido-2-deoxysugars in which it is possible to isolate the following principal stages[63]: protection of the amino-group with the aid of anisaldehyde, exhaustive *O*-acetylation with acetic anhydride in pyridine, removal of the anisidine protection group, and condensation of the acetyl-substituted aminosugar with alkyl or aryl isocyanates. Treatment of the *O*-acetyl-substituted condensation products with an ammoniacal solution of methanol permits smooth deacetylation and the preparation of the unsubstituted derivatives of 2-ureido-2-deoxysugars:

Scheme 8





The bond lengths (Å) and valence angles (degrees) in *N*-methyl-*N*-β-D-xylopranosylurea. The oxygen atoms of the neighbouring groups forming hydrogen bonds with the given molecule (dashed lines) are also shown.

III. THE STRUCTURE AND PROPERTIES OF *N*-GLYCOSYLUREAS

The structure and properties of *N*-glycosylureas have been most thoroughly studied among ureidosugars. The structures of *N*-glycosylureas, demonstrated with the aid of traditional methods of carbohydrate chemistry—periodate oxidation, exhaustive acrylation, acid hydrolysis, and specific synthesis by the isocyanate method—have been described in a review[4]. In the vast majority of the known ureidosugars the carbohydrate residue exists in the cyclic, principally the pyranose form with a 1,2-*trans*-glycosidic linkage[24].

An X-ray diffraction study of *N*-methyl-*N'*-β-D-xylopyranosylurea showed[64] that the carbohydrate ring is in the $C_{(1)}$ conformation, while the carbamide residue has an almost planar trigonal structure (see Figure). The plane of the carbamide residue forms a dihedral angle of 4.5° with the plane of the carbohydrate ring. The valence angles at the atoms of the pyranose ring are close to the tetrahedral value, while the bond lengths are close to the standard $C(sp^3)$–$C(sp^3)$ and $C(sp^3)$–O bond lengths. The $C_{(8)}$–$N_{(7)}$ bond in the urea residue is somewhat lengthened, while the $C_{(8)}$–$N_{(9)}$ bond is somewhat shortened compared with the corresponding bonds in ureas.

The crystals of *N*-methyl-*N'*-β-D-xylopyranosylurea belong to the orthorhombic system ($P\ 2_12_12_1$ group): $a = 6.707$ Å; $b = 8.670$ Å; $c = 15.944$ Å; $\alpha_{calc} = 1.48$ g cm^{-3}; $Z = 4$. In the crystal lattice the molecules are "cross-linked" by hydrogen bonds and give rise to a two-dimensional network in the *ac* plane. Each molecule is involved in four intermolecular hydrogen bonds of the type O–H...O with participation of the OH groups at the $C_{(3)}$ (two bonds) and $C_{(4)}$ atoms as well as the C = O group of the urea residue. The hemiacetal oxygen ring atom and both NH groups are not involved in the system of hydrogen bonds. The hydrogen bonds apparently make the main contribution to the energy of the crystal[64].

The range 1400–1800 cm^{-1}, free from the absorption bands of the carbohydrate residues, is suitable for the identification of *N*-glycosylureas with unprotected OH groups on the basis of absorption spectra[65]. In this region there are characteristic "amide" absorption bands, which frequently make it possible to determine the nature of the substituents at the nitrogen atom (see Table). The band near 1560 cm^{-1}, which is associated with the deformation vibrations of the N–H bond ("the amide-II" band), is a reliable spectroscopic characteristic of the *N*-glycosidic linkage in *N*-glycosylureas. The absorption bands of free urea (at 1625 and 1680 cm^{-1}) do not change significantly when urea is incorporated into a monosaccharide. An absorption band at 1635–1645 cm^{-1} is characteristic of *N*,*N'*-diglycosylureas, while bands at 1630–1640 cm^{-1} (C = O) and 1585–1590 cm^{-1} (N–H) are characteristic of *N*-alkyl-substituted 2-ureido-2-deoxysugars[66]. The replacement of an alkyl substituent in these derivatives by a phenyl group shifts the stretching vibration frequency of the C = O group to 1690 cm^{-1} and lowers the frequency of the deformation vibrations of the N–H

bond to 1540 cm^{-1}. The introduction of a nitroso-group in the *N*-position results in a still greater shift (to 1710 to 1720 cm^{-1}) of the frequency of the C = O group in the -NH-CO-NHR fragment; at the same time the absorption band of the *N*-nitroso-group appears in the range 1450 to 1500 cm^{-1}. Acetylation of ureidosugars results in a marked levelling of the infrared spectra.

The characteristic signals of the anomeric proton and of the protons at the other carbon atoms of the carbohydrate skeleton in the NMR spectra are in general retained for *N*-glycosylureas and 2-ureido-2-deoxy-derivatives. The signal of the hydrogen atom linked to $C_{(1)}$ in the β-anomers of ureidosugars has a chemical shift δ = 6.00–6.34 p.p.m.; as a result of the interaction with the hydrogen atom at $C_{(2)}$, this signal is a doublet and the spin–spin coupling constant J = 9 Hz. The signals of the protons in the carbamide residue (-NH-CO-NH-) are in the range δ = 4.2–5.5 p.p.m. and, together with the signals of the protons of the carbohydrate ring, give rise to an extremely complex group whose complete analysis is possible at working frequencies of spectrometers in excess of 100 mHz.[66]

The "amide" absorption bands of certain *N*-glycosylureas and their derivatives.

Compound	Frequencies, cm^{-1}
N-β-D-Glucosylurea	1555, 1625, 1670
N-β-D-Galactosylurea	1565, 1635, 1663, 1680
N-β-D-Mannosylurea	1565, 1630, 1680
N-β-D-Xylosylurea	1560, 1615, 1680
N,N Di-D-mannosylurea	1575, 1650
N,N'-Di-D-xylosylurea	1585, 1645
N-Methyl-*N'*-β-D-glucosylurea	1572, 1672
N-Phenyl-*N'*-β-D-glucosylurea	1560, 1660
Urea	1629, 1681
N-Methylurea	1580, 1660
N,N-Dimethylurea	1530, 1634, 1680

The introduction of the carbamide *N*-aglycone leads to an appreciable decrease of the reactivity of the glycosidic centre in relation to nucleophiles without altering significantly the properties of the OH groups of the carbohydrate skeleton and the functional groups of the urea residue. Glycosylureas are stable in dilute solutions of acids and alkali and hydrolyse only in a highly acid medium.

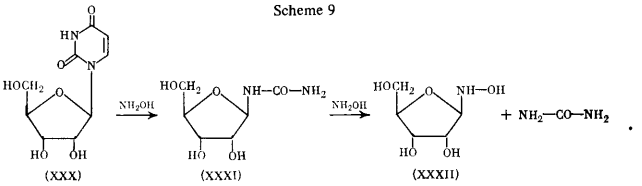
Glycosylureas give a negative response on treatment with reagents for the aldehyde group. In contrast to *N*-glycosides with aglycones of moderate and high basicity ($pK_a \cong 2-10$), glycosylureas do not enter into transamination (*N*-transglycosylation), osazone formation, and anomerisation reactions and do not undergo the Amadori rearrangement under the conditions of the acid–base catalysis typical for these reactions[2,3]. However, it has been shown[27] that heating of tetra-*O*-acetyl-*N*-β-D-glucopyranosylurea in glacial acetic acid leads to the formation of an equilibrium mixture of anomers with approximately 14.5% of the α-anomer.

The reactivity of the glycosidic centre in sugars in relation to nucleophiles is determined by the effective positive charge on the $C_{(1)}$ atom, so that all the factors promoting an increase of the positive charge favour nucleophilic addition and substitution reactions. Such factors include acid catalysis, whose mechanism is described satisfactorily on the basis of the idea that the heteroatom in the glycosidic linkage is protonated.

The rate of the acid-catalysed nucleophilic reaction involving $C_{(1)}$ should increase with increasing basicity (pK_a) of the *N*-aglycone, which agrees with the results of kinetic studies[2]. The replacement of the oxygen atom in monosaccharides and *O*-glycosides by the more basic nitrogen atom in the *N*-glycosidic linkage increases, other experimental conditions being equal, the probability of the protonation of the glycosidic linkage and hence also the rate of nucleophilic reactions involving the $C_{(1)}$ atom. As regards glycosylureas, the pK_a for the basicity of the nitrogen atom involved in the *N*-glycosidic linkage is very low ($pK_a \cong 0.1$) compared with *N*-aryl- and *N*-alkyl-glycosides. The probability of its protonation in moderately acid media is therefore very low. Furthermore, calculations have shown[67,68] that the most probable site of the protonation of urea is the oxygen atom. The protonation of the oxygen atom is energetically favourable, but it does not promote and actually lowers the reactivity of the $C_{(1)}$ centre owing to the decrease of the probability of the protonation of the nitrogen atom of the *N*-glycosidic linkage.

The above factors can account for the relatively high hydrolytic stability and low reactivity of glycosylureas in nucleophilic substitution reactions. In this respect the $C_{(1)}$–N bond in glycosylureas has properties approaching those of the *N*-glycosidic linkages in pyrimidine nucleosides and their analogues. For example, it is instructive that, in the hydroxylaminolysis of cytosine and uracil nucleosides, the heterocycle is the first to be cleaved, the *N*-aglycone being displaced from *N*-β-D-ribofuranosylurea (XXXI) only in the concluding stages of the reaction under fairly severe conditions (see the scheme below):[69]

Scheme 9



(XXX) (XXXI) (XXXII)

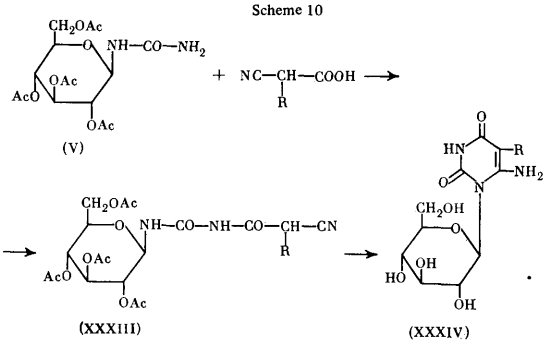
IV. THE REACTIONS OF UREIDOSUGARS AND THE SYNTHESES ON THEIR BASIS

1. The Synthesis of Nucleosides and Their Analogues

Glycosylureas and glycosylthioureas can serve as the starting materials for the synthesis of *N*-glycosides of the pyrimidine series by the cyclisation of the carbamide aglycone on the basis of the known reactions for the formation of pyrimidine systems. One of the first studies in this field was that of Goodman[70], who described the synthesis of 6-amino-*N*-β-D-glucopyranosyluracil (XXXIV) by the Trauber reaction involving the treatment of tetra-*O*-acetyl-β-D-glucopyranosylurea (V) with cyanoacetic acid and subsequent deacetylation of the condensation product (XXXIII) with an ethanol solution of ammonia. The removal of the acetyl protecting groups resulted also in the simultaneous cyclisation of the *N*-aglycone. Goodman obtained in this way a series

of alkyl- and aryl-substituted glucosyl derivatives of 6-aminouracil:

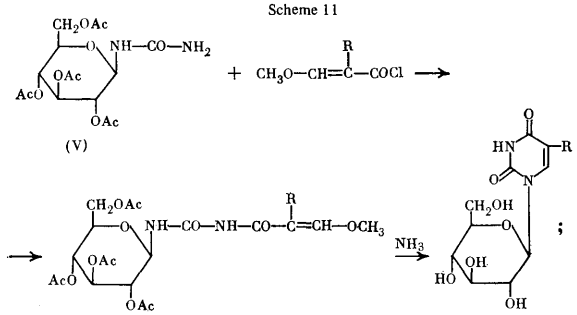
Scheme 10



(V) (XXXIII) (XXXIV)

Japanese investigators[71-76] synthesised pyrimidine *N*-glycosides by the condensation of fully *O*-acetylated *N*-glycosylureas and glycosylthioureas with the chlorides of acrylic and methacrylic acids. Thus β-D-glucopyranosylthymine (XXXVI) has been obtained by the reaction of tetra-*O*-acetyl-β-D-glucopyranosylurea (V) with 3-methoxy-2-methacrylic acid chloride and treatment of the condensation product, tetra-*O*-acetyl-β-D-glucopyranosyl-3-(3-methoxy-2-methylacryloyl)urea (XXXV), with a 3.3% solution of ammonia at 80 °C for 2 h. Under these conditions, the carbohydrate residue is deacetylated and the *N*-aglycone cyclises via Scheme 11. β-D-Arabinopyranosylthymine has been obtained analogously.

Scheme 11

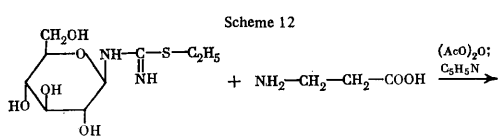


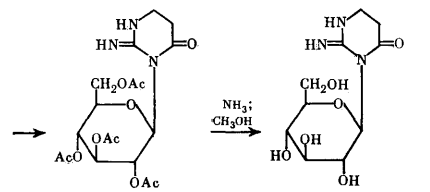
(V) (XXXV) R = CH_3. (XXXVI)

In these syntheses the yields of products reach 60–70% in the stage involving the condensation of the acid chloride with *O*-acetylated glycosylureas and 60% in the stage where the intermediate is deacetylated and cyclises. In terms of efficiency, the above method of synthesis of glycosylthymines is comparable to the method of Ralph and Shaw, which is based on the interaction of α-cyano-β-ethoxycarbonylacrylamide with glycosylamines (see Shabarov's review[77]).

Micheel and coworkers[57,58] synthesised analogues of nucleosides and *N*-glycosides with heterocyclic aglycones using *N*-glycosylthioureas. Thus the glycosyl derivative of hexahydropyrimidine (XXXVIII) has been obtained from *S*-ethyl-*N*-β-D-glucopyranosylthiourea via the following scheme:

Scheme 12





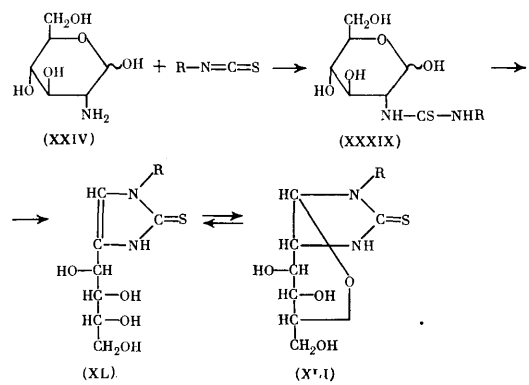
(XXXVII) (XXXVIII)

2. Reactions Involving Neighbouring Groups

In modern carbohydrate chemistry reactions with neighbouring group participation are used to invert the configuration of the carbon atoms and for the stereospecific synthesis of glycosides[1-5,78,79]. Under the conditions of acid catalysis, the collaboration effects frequently lead to migration of the functional groups to neighbouring carbon atoms via intermediate stages involving the formation of acetoxonium, oxazoline, and other heterocycles in the carbohydrate chain. An analogous picture has been observed also for ureidosugars.

The effect of the collaboration of the neighbouring groups in *O*-substituted sugars has been examined in detail[80] in relation to nucleophilic reactions of $C_{(1)}$-acetyl derivatives of sugars. Subsequently the ideas concerning the mechanism of the intramolecular reactions of neighbouring groups were developed by Lemieux[78], but, long before these studies, Neuberth and Wolf[81] established in 1901 that the reaction of D-glucosamine with allyl and phenyl isothiocyanates leads to the formation of stable derivatives of imidazoline-2-thione (XL) (see Scheme 13). It was later shown[82,83] by periodate oxidation and acetylation methods that the condensation product exists in the glucopyranose form (XLI) and it has been observed[84] that in alcoholic solutions the interaction of D-glucosamine with isothiocyanates leads initially to the formation of derivatives of 2-thioureido-2-deoxy-D-glucose (XXXIX), which then undergo an intramolecular cyclisation on treatment with glacial acetic acid with formation of the heterocycle (XL). The interaction of isothiocyanates with products of the Amadori rearrangement leads to analogous derivatives[85].

Scheme 13

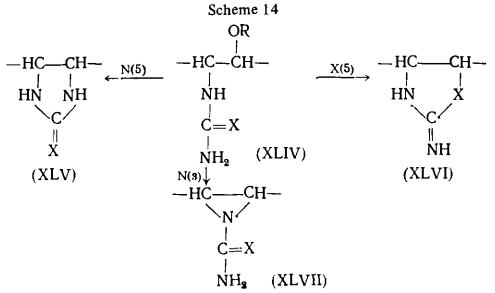


(XXIV) (XXXIX) (XL) (XLI)

Intramolecular cyclisation of the carbamide and thiocarbamide fragments in a series of alkyl(or aryl)-2-thioureido(or 2-ureido)-2-deoxy-D-glucopyranose yielded[63] a large number of derivatives of 3-alkyl(aryl)-1-aryl-4-(D-arabinotetrahydroxybutyl)-imidazolin-2-ones (imidazoline-2-thiones) (XL).

The mechanism of the collaboration process can be represented by a scheme which provides for intramolecular nucleophilic attack by the heteroatom of the functional group on a neighbouring carbon atom linked to a readily removed substituent (see Scheme 14). The carbamide substituents in general possess three potentially active nucleophilic centres capable of involvement in intramolecular substitution processes. Depending on which of the three centres attacks a neighbouring *trans*-substituent, there is a possibility of $N_{(5)}$-cyclisation with formation of the imidazole ring compound (XLV), $X_{(5)}$-cyclisation accompanied by the formation of heterocyclic structures of the type of (XLVI), and $N_{(3)}$-cyclisation leading to the closure of the aziridine ring (XLVII).

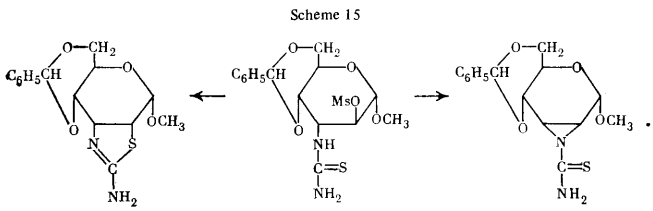
Scheme 14



(XLV) (XLIV) (XLVI) (XLVII)

In a series of studies[86-93] on the synthesis of analogues of nucleosides, reactions with involvement of carbamide[90-92], thiocarbamide[89,92-93] and guanidine[88-91] fragments were investigated in detail and empirical rules were formulated for the determination of the preferential mode of intramolecular cyclisation as a function of the positions of the attacking and leaving (sulphonate ester) groups and the basicity of the medium. As an example, one may quote reactions involving intramolecular substitution in the molecule of methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-methanesulphonyl-3-thioureido-α-D-altropyranoside (XLVIII). When compound (XLVIII) is kept in boiling pyridine for 1 h, a product with the thiazoline structure (XLIX) is formed in yields up to 70%. When it is treated with sodium methoxide, cyclisation with formation of the aziridine structure (L) takes place:

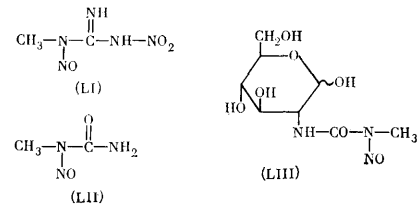
Scheme 15



(XLIX) (XLVIII) (L)

3. Carbohydrate Derivatives of *N*-Alkyl-*N*-Nitrosoureas

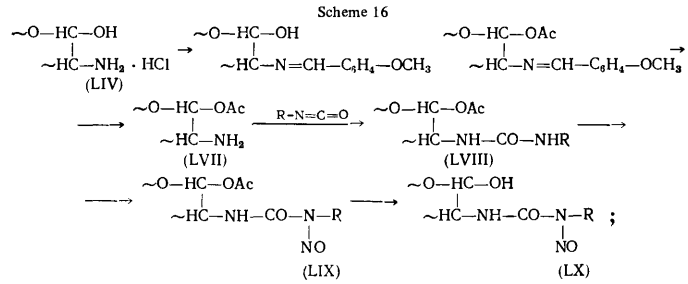
Sugar derivatives with *N*-alkyl-*N*-nitrosocarbamide fragments merit special consideration in view of their exceptionally important role in the chemotherapy of cancer[15,94]. Interest in compounds of this class arose at the beginning of the 1960s after the discovery of the high antileukaemic activity of 1-methyl-1-nitroso-3-nitroguanidine (LI) [95] and 1-methyl-1-nitrosourea (LII).[96] During the same years, the antibiotic streptozotocin was isolated from the culture liquid of streptomycin[97-101] and its structure was then readily demonstrated by specific synthesis from tetra-*O*-acetyl-D-glucosamine and methyl isocyanate with subsequent nitrosation and deacetylation of the condensation product[101]:



(LI) (LII) (LIII)

The preparative syntheses of a number of *N*-alkyl-substituted analogues of streptozotocin via Scheme 16 have been achieved[66,101,102].

Scheme 16



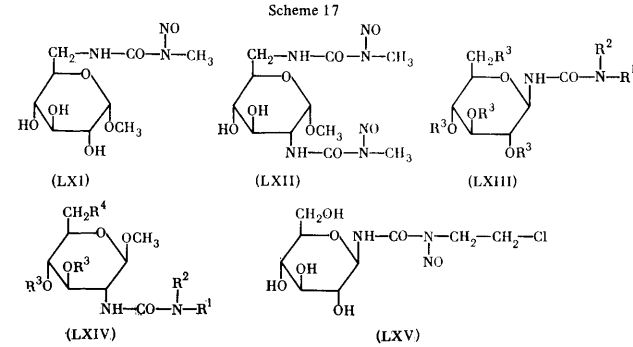
(LIV) (LVII) (LVIII) (LIX) (LX)

R=CH_3, C_2H_5, C_3H_7, C_4H_9 .

The discovery of streptozotocin and the determination of the spectrum of its therapeutic activity (antibiotic, antitumour, etc.) stimulated experimental research into the synthesis of a wide variety of carbohydrate-containing *N*-nitrosoureas as well as tests on their biological activity. In the search for syntheses of selectively acting antitumour agents with a high solubility and a low toxicity, methods of synthesis were developed during a comparatively short time for *N*-nitroso-derivatives of ureidosugars with various locations of the *N*-nitroso-carbamide fragments in the carbohydrate ring and with a wide variety of substituents and carbohydrate residues[103-117].

Japanese investigators achieved considerable successes in this field[104-111]. Derivatives of α-methyl-D-glucopyranoside with one [compound (LXI)] and two [compound (LXII)] methyl-*N*-nitrosocarbamide fragments, *N*-alkyl-*N*-nitroso-derivatives of *N*-β-D-glucosylurea (LXIII), and 1-methyl-β-D-glucosamine (LXIV) have been synthesised and their pharmacological activities have been largely tested (Scheme 17). The derivatives were synthesised by a fairly general method involving the interaction of glucosamine with alkyl isocyanates and nitrosation of the condensation products with sodium nitrite in acetic acid solutions.

Scheme 17



(LXI) (LXII) (LXIII) (LXIV) (LXV)

R′—CH_3, C_2H_5, C_3H_7, C_4H_9; R^2=H, NO; R^3=OH, OAc;
R^4=H, OH, OAc, OMs, NH—CO—N (NO) CH_3 .

It has been shown[118] that the replacement of the CH_3 group in *N*-methyl-*N*-nitrosurea by the 2-chloroethyl fragment increases the antitumour activity in relation to leukaemia; later, monosaccharide derivatives of 1-(2-chloroethyl)-3-(D-glucosyl)urea (LXV) were synthesised and preliminary tests on their antitumour activities were performed[110,119–122].

Comparative pharmacotoxicological studies established[123] that the addition of *N*-methyl-*N*-nitrosourea to the glycosidic centre in unprotected monosaccharides leads to a sharp decrease of the toxicity of the antitumour preparation and to a change of the spectrum of its action in relation to a number of experimental tumour models. It has also been shown that the toxicity and selectivity of the action of carbohydrate analogues of methylnitrosourea depend significantly on the nature of the monosaccharide carrier of the cytotoxic agent. This leads to the possibility for the specific regulation of the pharmacological properties of anticancer preparations by altering the structure of the carbohydrate unit.

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Aminoacids as the Amine Component in the Mannich Reaction

A.G.Agababyan, G.A.Gevorgyan, and O.L.Mndzhoyan

The review is devoted to the aminomethylation of the CH-, NH-, and the PH-acid residues by aminoacids. Data are presented on the biological activities of certain Mannich bases derived from aminoacids.
The bibliography includes 132 references.

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V. Biological properties of Mannich bases derived from α-aminoacids 393

I. INTRODUCTION

Mannich aminomethylation consists in the compensation of the substrate R–H containing at least one active hydrogen atom (alkyl ketones, phenols, various heterocycles, etc.) with formaldehyde (more rarely with other aldehydes) and primary or secondary amines (or ammonia):

$$R{-}H + CH_2O + HN\langle \rightarrow R{-}CH_2{-}N\langle \quad .$$

The great flexibility in the choice of reagents, the wide variety of possibilities for other reactions of the Mannich bases, and mild conditions have made the Mannich reaction one of the important methods of modern organic chemistry.

There is an extensive literature on studies of the Mannich reaction, in particular fundamental reviews and monographs[1-7]. However, aminomethylation by aminoacids as a special case of this comprehensively investigated reaction has so far been inadequately dealt with in the literature.

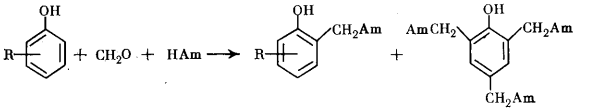
It is known that Mannich bases have a wide spectrum of biological activity[8]. Many of them have found applications in medicine. Thus the hydrochlorides of 4-(n-propoxy)- and 4-(n-butoxy)-β-piperidinopropiophenones (falicaine and dyclonine) are used as local anesthetics[9-11] and the hydrochloride of 4,α-dimethyl-β-piperidinopropiophenone (mydocalm) serves as an anticonvulsant[12]. Certain aminomethyl derivatives of tetracycline (morphocycline, glycocycline, lymecycline) are used in medical practice together with other tetracyclines[13,14]. Antibacterial activity has been observed also in many other Mannich bases[15-19].

The results of studies during the last 10–15 years indicate anti-inflammatory and pyretic[20,21], spasmolytic[22], adrenolytic[23], H-cholinolytic[12,23-25], and analgesic[26-28] properties of aminomethyl derivatives of ketones, phenols, and various heterocycles. Certain coumarin derivatives stimulate the activity of the respiratory and nervous systems[29]. On the other hand, aminoacids, being an inseparable component of the living organism, have become recently the subject of profound investigation from the standpoint of biological properties. Among synthetic derivatives of aminoacids, anti-inflammatory, antipyretic[30-38], antiviral and antibacterial[32,34,39-46], hypotensive[47-53], anti-tumour[32,36,38,46,54-57], and analgesic[33] substances as well as substances acting on the surface nervous system[34,58,59] have been found. As a consequence of this, the biological properties of Mannich bases obtained when the amino-residue is replaced by an aminoacid residue are of special interest.

The aim of the present review is to survey the available literature data on the aminomethylation of various organic compounds by aminoacids in particular CH-, NH-, and PH-acid residues as well as the data on the biological activity of certain Mannich bases derived from aminoacids.

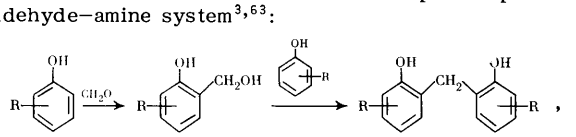
II. AMINOMETHYLATION OF CH-ACID RESIDUES

The first communications on aminomethylation by aminoacids refer to phenols[60,61].† When phenols were condensed with formaldehyde and aminoacids, both the usual aminomethyl derivatives of phenols (I, a and b) and polymeric compounds with benzene rings linked by methylene groups were obtained[60]:

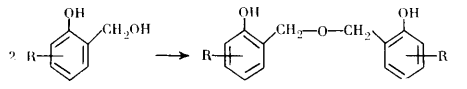


Am = Gly, Ala, Leu, and other aminoacids.

Bearing in mind that phenols are capable of condensing with formaldehyde, apart from the Mannich reaction it is necessary to consider a further two possible pathways [reactions (1) and (2)] in the three-component phenol–formaldehyde–amine system[3,63]:



(1)

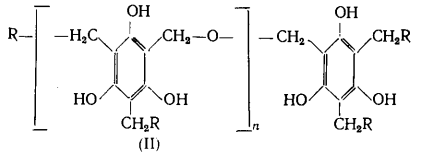


(2)

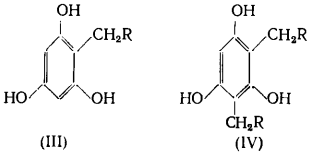
† The Mannich reaction between phenol, iminodiacetic acid, and formaldehyde has also been investigated[62].

Scheme (1) explains the formation of polymeric compounds described in a patent[60].

Later a reaction between aminoacids[64] (particularly glycine), polyhydric phenols, and formaldehydes was investigated#. It has been shown on the basis of ultraviolet and infrared spectroscopic data that the most probable structure of the condensation product is (II):



(II)



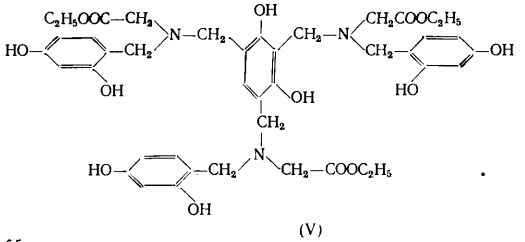
(III) (IV)

R=NHCH$_2$COOH

Structure (II) corresponds to the condensation product of phloroglucinol, glycine, and formaldehyde taken in proportions of 1:2:6. The possibility of the formation of products (III) and (IV) has also been demonstrated.

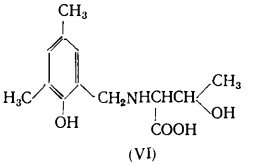
Apart from glycine, other aminoacids as well as di- and tri-peptides have also condensed with phloroglucinol. Thus, according to Gringras and Sjostedt[64], glycine and lycine react with phloroglucinol and formaldehyde to the extent of 90%, the degree of reaction of aspartic acid is 70%, while alanine and leucine react to the extent of 50%.

Data have been published[61] on the aminomethylation of resorcinol by both amines and aminoacid derivatives. In contrast to piperidine and morpholine which led to trisaminomethyl derivatives of type (Ib), ethyl glycinate reacts with resorcinol and formaldehyde to form a product with the tentative structure (V):



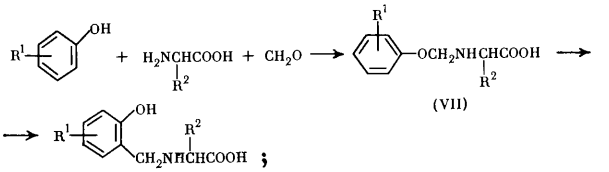
(V)

Blass[65] reported the synthesis of the Mannich base (VI)—a derivative of threonine and 2,4-dimethylphenol (yield 67%):

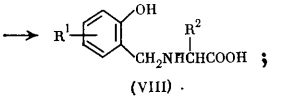


(VI)

As expected, substitution takes place at the *o*-carbon atom of the benzene ring. It has been suggested[66-68] that the aminomethylation takes place initially at the phenolic hydroxyl with formation of the product (VII), which subsequently, on heating to 80–100 °C or under the influence of inorganic acids at 50–60 °C, isomerises to the *C*-aminomethyl derivative (VIII):



(VII)

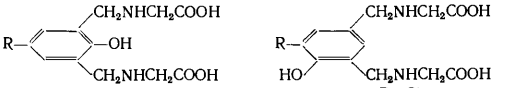


(VIII).

R^2=H; R^1= *p*-Cl, *p*-Br, or *o*-(*m*-, *p*-)OH;
R^2=CH$_3$; R^1=H, *o*-(*m*-, *p*-)CH$_3$, *p*-iso-C$_3$H$_7$, *p*-t-C$_4$H$_9$, or *p*-t-C$_5$H$_{11}$.

However, this mechanism was not confirmed in subsequent studies[69,70].

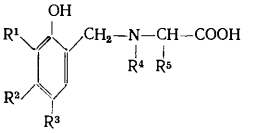
In the presence of a twofold excess of formaldehyde and glycine, 2,6- and 4,6-bis(carboxymethylaminomethyl)phenols (IX) were obtained[68]:



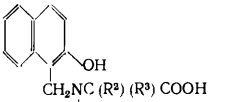
(IXa), R=Br, or F (IXb), R=Cl, or I

2,4,6-Trihalogenophenols and *o*-nitrophenol do not undergo the Mannich reaction with aminoacids under these conditions[68].

The synthesis of Mannich bases derived from phenols, naphthols, and certain aminoacids has been described[71]:



(X)



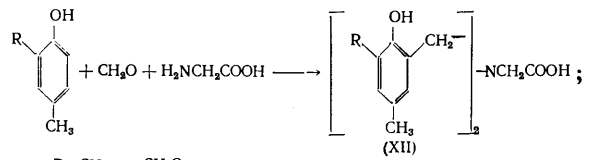
(XI)

(a) R^1=H, R^2=CH$_3$O; R^3=OH; R^4=H, or CH$_3$; R^5=H, or CH$_2$CH$_2$SCH$_3$;
(b) R^1=CH$_3$; R^2=H; R^3=CH$_3$; R^4=H, or CH$_3$, R^5=H, CH$_3$, CH$_2$COOH, CH$_2$OH, or CH$_2$CH$_2$SCH$_3$;
(c) R^1=CH$_3$O; R^2=R^5=H; R^3=CH$_3$, CHO, COOH, or CH$_3$O; R^4=H, or CH$_3$;
(d) R^1=Cl; R^2=R^5=H; R^3=Cl, R^4=CH$_3$.

(a) R^1=H; R^2=CH$_3$, or CH$_2$OH R^3=H, or CH$_3$;
(b) R^1=CH$_3$; R^2=R^3=H.

The authors showed that 2,4-dimethylphenol reacts with formaldehyde and a number of aminoacids (glycine, glutamic acid, alanine, serine, and methionine) to form *N*-benzyl derivatives. Sarcosine condenses successfully with formaldehyde and 2,4-dimethyl-, 2-methoxy-4-methyl-, and 2,4-dichlorophenols.

The reaction of glycine and formaldehyde with 2,4-dimethyl- and 2-methoxy-4-methyl-phenols leads to *N*,*N*-bisbenzyl derivatives (XII)[71]:



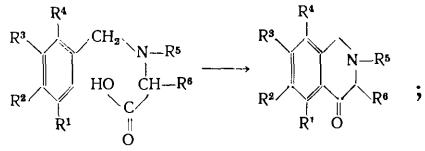
(XII)

R=CH$_3$, or CH$_3$O.

N-Benzylaminoacids (XIII) have been cyclised to derivatives of 1,2-dihydro-4(3*H*)-isoquinolone (XIV)[72]. In particular *N*-(2-hydroxy-3-methoxy-5-methylbenzyl)sarcosine (XIII)

On the basis of the similarity of the ultraviolet spectra of "cross-linked" ("bridged") products formed from gelatin and the products of the Mannich reaction involving aminoacids and peptides, the authors[64] concluded that the reaction mechanisms are similar.

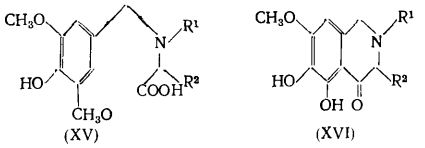
readily cyclises in the presence of sulphuric acid to form 1,2-dihydro-8-hydroxy-7-methoxy-2,5-dimethyl-4(3*H*)-isoquinolone (XIV):



(XIII) (XIV)

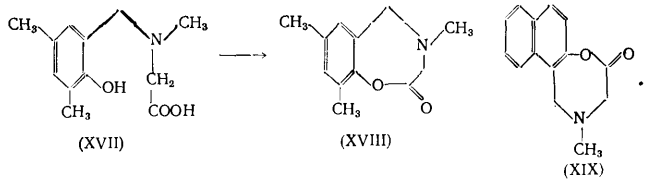
$R^1=R^5=CH_3$; $R^2=R^6=H$; $R^3=CH_3O$, $R^4=OH$.

In the cyclisation of *N*-(4-hydroxybenzyl-3,5-dimethoxy)-sarcosine (XV, $R^1 = CH$, $R^2 = H$) and *N*-(4-hydroxybenzyl-3,5-dimethoxy)alanine (XV, $R^1 = H$, $R^2 = CH_3$) the methoxy-group in the 3-position hydrolyses simultaneously with formation of compound (XVI):



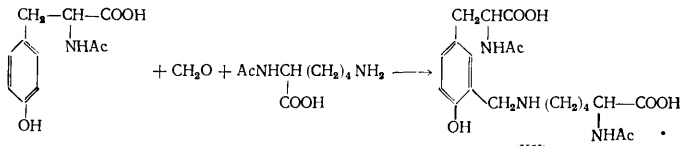
(XV) (XVI)

ortho-Substituted phenolic Mannich bases of type (XVII) are capable of being lactonised in the presence of thionyl chloride with formation of benzoxazepins (XVIII). 1,2-Dihydro-2-methylnaphtho[1,2-*f*]-1,4-oxazepin-4(3*H*)-one (XIX) has been obtained in a similar fashion to compound (XVIII)[72]:



(XVII) (XVIII) (XIX)

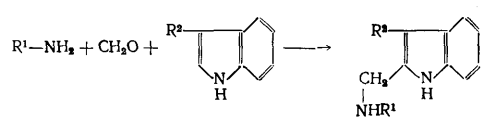
Sometimes the aminoacid itself can serve as the CH-acid component. Thus tyrosine, being a phenol derivative, condenses with formaldehyde and lycine to form the "bridged" compound (XX): Lys-CH_2-Tyr[73] (the α-amino-groups of both aminoacids are protected):



(XX)

The above interaction of aminoacids with formaldehyde and phenol[65] can be regarded as a model of this type of reaction (aminoacid-1-formaldehyde-aminoacid-2). A series of model "cross-linked" systems have been obtained[74,75]. 2,4-Dimethylphenol (model of tyrosine), 3-methylindole§ (model of tryptophan), and alkylamides¶ (models of glutamine and asparagine) have been used as models of aminoacids.

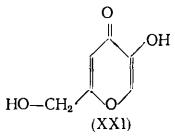
§ However, the indole fragment of tryptophan undergoes the Mannich condensation predominantly as the CH-acid component[77]:



¶ See the next Section for the details of the interaction of aminoacids with amides.

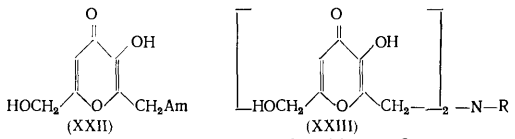
The position of the methylene group has been determined by ^{13}C NMR, which constitutes a convenient non-destructive method for the determination of the location of cross links in peptides treated with formaldehyde.

Thus the possibility of using the Mannich reaction for the synthesis of *C*-aminomethyl compounds in which the amino-fragment is an aminoacid has been demonstrated in relation to phenols. However, it has been suggested[76] that the aminomethylation of phenols by aminoacids involves experimental difficulties (long reaction time and the difficulty of isolating the final products) and cannot be used to synthesise the corresponding aminomethyl derivatives. Nevertheless it was shown[76] that kojic acid (5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one) (XXI), which is structurally similar to phenol, can be successfully condensed with formaldehyde and a number of aminoacids: glycine, sarcosine, valine, leucine, isoleucine, methionine, and taurine.



(XXI)

The formation of the mono-derivative (XXII) has been noted for all the aminoacids investigated; glycine and taurine, in which both amino-hydrogen atoms are substituted with formation of compound (XXIII), are an exception:



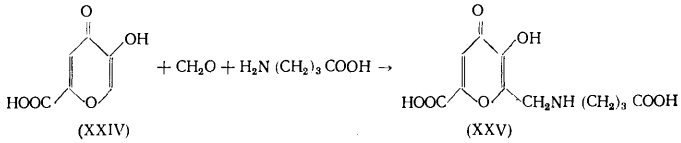
(XXII) (XXIII)

R=CH_2COOH, or $(CH_2)_2SO_3H$.

As was to be expected, aminoacids of different structures condense with formaldehyde and CH-acid components with different degrees of ease. The best results have been achieved in the aminomethylation of kojic acid by valine: heating for 50 min leads to an 80% yield of the final product[76]. This finding and also the lack of differences in the aminomethylation with leucine and isoleucine can be readily accounted for by steric factors.

O'Brien et al.[76] were unable to obtain the aminomethyl derivatives of kojic acid with asparagine, glutamine, aspartic, and glutamic acids, phenylalanine, and tyrosine. They believe that the main reason for the failure of the reaction with phenylalanine and tyrosine is their insolubility in the reaction mixture. In the case of dibasic acids (glutamic and aspartic) the second carboxy-group apparently exerts an inhibiting influence.

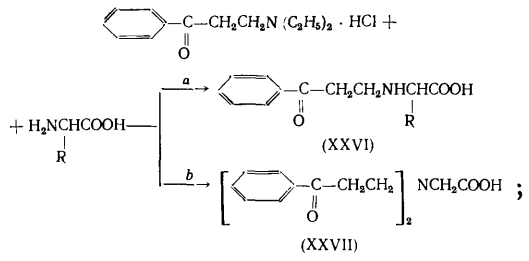
The aminomethyl derivative (XXV) has been obtained by the condensation of γ-aminobutyric acid with formaldehyde and comenic acid (XXIV)[78]:



(XXIV) (XXV)

There are contradictory data in the literature on the aminomethylation of acetophenones. Thus it has been suggested[79] that the Mannich reaction with acetophenones and α-aminoacids hardly occurs and the corresponding aminomethyl

derivatives (XXVI) and (XXVII) have been obtained by the reaction

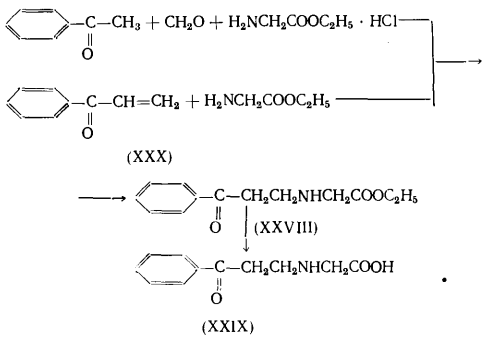


(XXVI)

(XXVII)

a:R=CH_3, CH_2COOH, CH_2CONH_2, $CH_2C_6H_5$;
b:R=H.

However, the ethyl ester[80] of *N*-β-benzoylethylglycine (XXVIII) has been obtained (albeit with a low yield) by the direct condensation of acetophenone, formaldehyde, and the hydrochloride of ethyl glycinate:



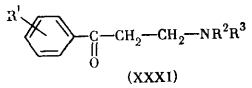
(XXX)

(XXVIII)

(XXIX)

N-β-Benzylethylglycine (XXIX) has been obtained by the hydrolysis of compound (XXVIII). Both products have also been synthesised by specific synthesis from acrylophenone (XXX) and glycine or its ethyl ester[80].

Although one of the convenient methods of synthesising β-aminoketones (derived from α-aminoacids) is in fact the Mannich reaction, many β-substituted aminopropiophenones having the general formula (XXXI) have been obtained by an exchange reaction[81]. The possibility of the aminomethylation of acetophenones by aminoacids via the Mannich reaction has been demonstrated only in relation to *N*-[β-(*o*-hydroxybenzoyl)ethyl]glycine[81]:

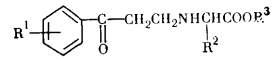


(XXXI)

(a) R^2=H; R^3=CH_2COOH; R^1 = *o*-HO, *o*-NH_2, *o*-CH_3O, *o*-C_3H_7O, *o*-iso-C_3H_7O, or *o*-(*m*-, *p*-)C_4H_9O;
(b) R^2=H; R^3=CH (CH_3) COOH (L-, DL-), CH ($CH_2CH_2SCH_3$) COOH (D-, L-, DL-), or CH (CH_2OH) COOH (L-, DL-); R^1 = *o*-HO; *o*-NH_2^*,
(c) R^2=H; R^3=CH [CH (CH_3)$_2$] COOH (D-, L-); R^1=*o*-HO (DL-); *o*-HO, *o*-CH_3O, *p*-Cl, *o*-(*m*-, *p*-)NH_2^*, CH_3CONH^*, *m*-(*p*-)CH_3NH^*, *p*-$C_4H_9NH^*$, *p*-CH_3COO^*, or *o*-(*m*-)Cl^*;
(d) R^2=H; R^3=C (CH_3) ($CH_2CH_2SCH_3$) COOH (DL-); R^1 = *o*-HO, or *p*-HO^*;
(e) R^2=H; R^3=CH [CH_2CH (CH_3)$_2$] COOH (D-, L-); R^1=*o*-HO, *p*-CH_3CONH^*, or *p*-$C_3H_7CONH^*$;
(f) R^2=H; R^3=CH [CH (OH) CH_3] COOH (D-, L-, DL-); R^1 = *o*-HO, *o*-NH_2^*, or *p*-iso-$C_3H_7O^*$;
(g) R^2=H; R^3=CH (CH_2) $CH_2SCH_2CH_3$) COOH (DL-); R^1 = *o*-HO, or *o*-CH_3O^*;
(h) R^2=CH_3; R^3=CH_2COOH; R^1 = *o*-(*m*-)HO, *m*-C_2H_5O, or *p*-C_3H_7COO;
(i) R^2=CH_3; R^3=CH [CH (CH_3)$_2$] COOH; R^1 = *p*-CH_3O^*;
(j) R^2=CH_3; R^3=CH [CH_2CH (CH_3)$_2$] COOH; R^1 = *o*-HO^*;
(k) R^2=C_2H_5; R^3=CH_2COOH; R^1 = *o*-HO;
(l) R^2 = iso-C_3H_7; R^3=CH [CH_2CH (CH_3)$_2$] COOH; R^1 = *o*-HO^*;
(m) R^2=C_4H_9; R^3=CH_2COOH; R^1 = *o*-HO.

† The optical forms of the aminoacid residues are not indicated.

Certain β-aminoketones (XXXII) derived from glycine, alanine, and valine have been synthesised by the Mannich condensation[71]:

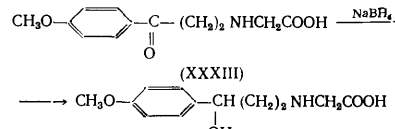


(XXXII)

(a) R^1=R^2=H, R^3=C_2H_5;
(b) R^1=4-CH_3O, R^2=H, CH_3, or (CH_3)$_2$ CH, R^3=H;
(c) R^1=4-HO-3-CH_3O, R^2=H, R^3=C_2H_5;
(d) R^1=3-NO_2, R^2=H, R^3=CH_3;
(e) R^1=3, 4, 5-(CH_3O)$_3$, R^2= H, R^3=C_2H_5 .

The authors achieved the best results using a mixture of cyclohexane and t-butyl alcohol as the solvent.

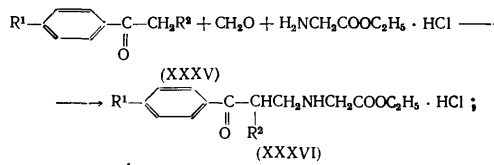
N-[β-(*p*-methoxybenzoyl)ethyl]glycine (XXXIII), obtained by the hydrolysis of the ethyl ester (XXXII, R^1 = 4-CH_3O, R^2 = H, R^3 = C_2H_5), was reduced with sodium tetrahydroborate to the corresponding alcohol (XXXIV)[71]:



(XXXIII)

(XXXIV)

The ethyl esters of *N*-(β-benzoylethyl)-, *N*-[β-(*p*-alkoxybenzoyl)ethyl]-, and *N*-[β-(*p*-halogenobenzoyl)ethyl]-glycines (XXXVIa, R^2 = H) and α-phenyl derivatives of some of them (XXXVIb, R^2 = C_6H_5) have been obtained by the condensation of 4-substituted acetophenones and benzyl phenyl ketones (XXXV) with formaldehyde and ethyl glycinate[82,83]:

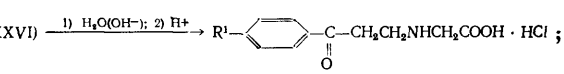


(XXXV)

(XXXVI)

R^1 = H, Alkyl, Cl, or Br.

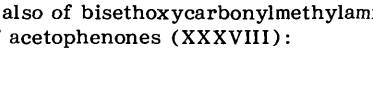
A number of *N*-[β-(*p*-alkoxybenzoyl)ethyl]glycines (XXXVII) have been synthesised by the hydrolysis of the corresponding ethyl esters (XXXVI)[82]:



(XXXVII)

R^2=H, R^1=H, or alkoxy.

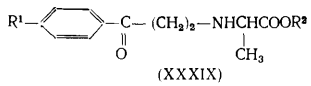
The authors[82] concluded that the aminomethylation of acetophenones with free glycine, as shown by Cymerman-Craig et al.,[79] does not in fact occur. However, condensation with the hydrochloride of ethyl glycinate instead of the free acid takes place in 20–30% yield. It has been shown that, apart from compound (XXXVI), the reaction leads to the formation also of bisethoxycarbonylmethylaminomethyl derivatives of acetophenones (XXXVIII):



(XXXVIII)

Agababyan et al.[83] published data on the aminomethylation of 4-substituted acetophenones with α-alanine. It was shown that, depending on the reaction conditions and the

reactant ratio, the yields of the aminoketones (XXXIX) vary significantly:

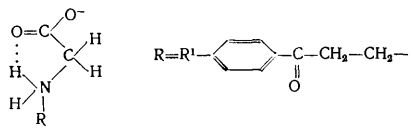


(XXXIX)

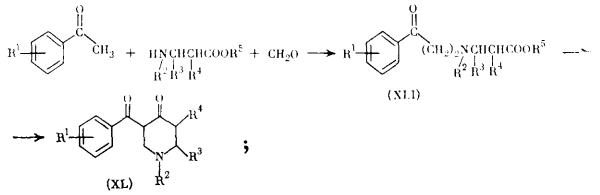
(a) R^2=H; R^1=H, CH_3O, C_2H_5O, C_3H_7O, iso-C_3H_7O, C_4H_9O, Cl, or Br;
(b) R^2=C_2H_5; R^1=C_3H_7O.

Thus, after refluxing for 10 h in ethanol (1:1:1 ratios of the reactants comprising 4-substituted acetophenone, paraformaldehyde, and alanine) at pH 6–7, the yield of the reaction product does not exceed 10–12%, whereas at pH 1–2 and for the same reaction time the yield increases to 28–30%. A change in the reactant ratios (twofold excess of acetophenone and formaldehyde) increases the yields to 30% (at pH 6–7) and 50% (pH 1–2). The replacement of ethanol by dioxan and the use of iron(III) chloride as the catalyst did not increase the yield of the final product. Certain aminoketones (XXXIX, R^1 = H, Br, iso-C_3H_7, or n-C_4H_9) have also been obtained by an exchange reaction[83].

The infrared spectra of *N*-[β-(p-alkoxybenzoyl)ethyl]glycines, their hydrochlorides (XXXVII), and ethyl esters (XXXVIa) have been investigated[84]. It has been established that the secondary amino-group is present only in the esters. In the hydrochlorides (XXXIX) the ketone oxygen forms an intermolecular hydrogen bond with the hydroxy-group of the carboxyl. It has been shown that the length of the alkoxy-group does not affect the intramolecular and intermolecular interactions. It has been suggested that the aminoacid fragment has a cyclic structure:



The Mannich reaction between acetophenones and α-aminoacid esters has been described[85]. The condensation products were further cyclised with sodium hydride to 3-benzoyl-4-piperidinones (XL):



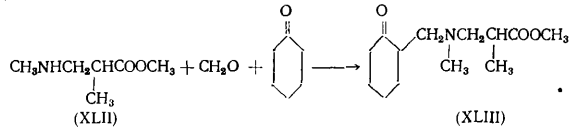
(XLI)

(XL)

(a) R^1=H, or CH_3O; R^2=CH_3, or C_2H_5; R^3=H, or CH_3; R^4=H, or CH_3; R^5=CH_3, or C_2H_5;
(b) R^1=CH_3; R^2=R^4=R^5=CH_3; R^3=H;
(c) R^1=Cl; R^2=R^3=CH_3; R^4=H; R^5=C_2H_5.

The stability of the ketoaminoesters (XLI) varies with their structure; *N*-methyl-substituted Mannich bases are more stable than the *N*-ethyl-substituted derivatives. It has been shown that esters with the methyl group in the α-position cyclise more readily than the esters with the methyl group in the β-position[85].

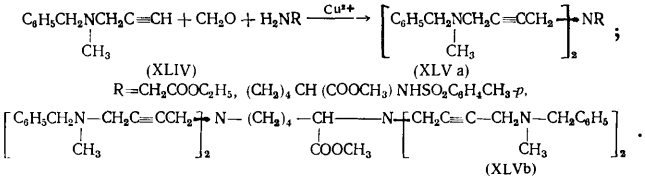
For comparison, a Mannich base has also been obtained from cyclohexanone and methyl β-methylaminopropionate (XLII)[85]:



(XLII) (XLIII)

However, the aminomethylation product (XLIII) could not be cyclised.

Acetylene derivatives have also been used as the CH-acid residues in the Mannich reaction. Aminomethylation of pargyline (*N*-methyl-*N*-propargylbenzylamine) (XLIV) with glycine or lysine derivatives yielded the corresponding Mannich bases (XLV)[86]:

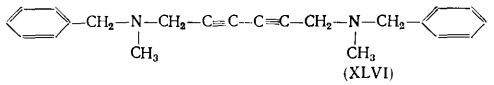


(XLIV) (XLV a)

R=$CH_2COOC_2H_5$, $(CH_2)_4CH(COOCH_3)NHSO_2C_6H_4CH_3$-*p*,

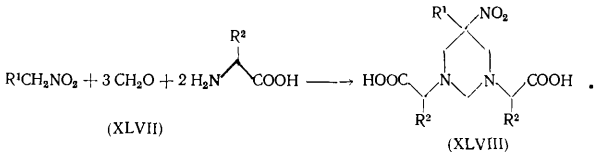
(XLVb)

The reaction was carried out at pH 6 in the presence of a catalyst—copper(II) chloride. At pH 9 or 4 pargyline does not react with the amino-component and formaldehyde, being oxidised to compound (XLVI):



(XLVI)

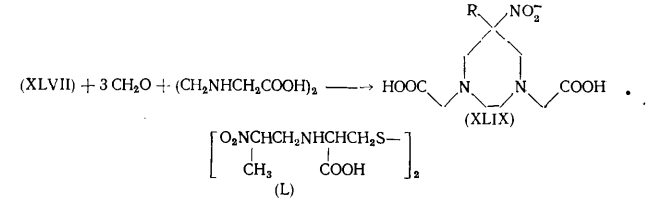
An interesting example of the Mannich reaction is that with nitroalkanes and aminoacids[87]. The hydrogen atoms in compound (XLVII) next to the nitro-group are very mobile, which promotes the cyclocondensation of this compound with two aminoacid molecules and three formaldehyde molecules to form the hexahydropyrimidine (XLVIII):



(XLVII) (XLVIII)

Glycine, β-alanine, valine, leucine, isoleucine, serine, threonine, phenylalanine, and methionine have been used successfully in this reaction (the lowest yield, in the reaction with phenylalanine, is 20%; in the remaining cases it is 60–80%).

In an analogous cyclisation reaction, Roth and Ergenzinger[87] obtained 6-nitro-1,4-diazacycloheptane-1,4-dicarboxylic acids (XLIX) from ethylenediamine-*N*,*N*′-diacetic acid. On the other hand, cysteine condenses with nitroethane and formaldehyde like a normal diamine, with formation of compound (L)—the "normal" Mannich base:



(XLIX)

(L)

However, cysteine does not undergo the Mannich condensation, since the reaction with formaldehyde leads to a cyclic product—thiazolidinecarboxylic acid[87,88].

III. AMINOMETHYLATION OF NH-ACID RESIDUES

Numerous studies[89–95] have been made on the interaction of aminoacids with formaldehyde and compounds containing nitrogen and mobile hydrogen atoms. This applied initially to the amine–formaldehyde–amide and amine–formaldehyde–guanidine coupling reactions, which have been studied by Fraenkel-Conrat and Olcott[91]. It was shown that, over a wide pH range at room temperature, formaldehyde can form

methylene bridges between the amino-group and the primary amide or guanidine NH_2 groups:

$$R^1{-}NH_2 + CH_2O + H_2N{-}C(=O){-}R^2 \longrightarrow RNH{-}CH_2{-}NH{-}C(=O){-}R^2 \ ;$$
$$R^1{-}NH_2 + CH_2O + H_2N{-}C(=NH){-}NHR^2 \longrightarrow RNH{-}CH_2{-}NH{-}C(=NH){-}NHR^2 \ . \qquad (3)$$

Neutral or acid media are preferable for reaction (3) between aminoacids and amides and between amines and amides respectively. The authors[91] explain this difference by the rapid formation of the cyclic trimers of the amines and formaldehyde in alkaline media. In order to confirm finally the condensation of aminoacids with formaldehyde and amides, the products of the interaction of alanine and proline with formaldehyde and acetamide were isolated.

Before the communication of Fraenkel-Conrat and Olcott[91], the mechanism of reaction (3) was studied inadequately. The authors[91] believe that, like the Mannich reaction, reaction (3) can be regarded as the condensation of a primary or secondary amine (in relation to alanine and proline), formaldehyde, and the NH-acid component—the primary amide group. According to Einhorn[96], an amidohydroxymethyl compound is formed initially. However, according to Fraenkel-Conrat and Olcott[91], despite the fact that the addition of formaldehyde to the primary amide group does indeed occur (this is also indicated by other data[94,95]), it is much slower than the "cross-linking" reaction, i.e. the formation of a methylene "bridge". It has been shown experimentally that the amidohydroxymethyl compound is incapable of subsequent condensation with the amine[91]. Thus reaction (3) proceeds in two stages:

$$R^1{-}NH_2 + CH_2O \xrightarrow{a} R^1NHCH_2OH \ ;$$
$$R^1NHCH_2OH + H_2NCOR^2 \xrightarrow{b} RNHCH_2NHCOR^2 + H_2O \ .$$

The interaction of the amino-group and the aminoacid with formaldehyde# is proved by a number of facts: the decrease of the pH of the reaction mixture and the change in the optical rotation of solutions of the L-aminoacid mixed with formaldehyde. The above two-stage mechanism is also confirmed by the change in the optical rotation of the mixture consisting of an optically inactive amide, an optically active amine, and formaldehyde[89].

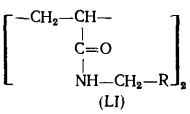
Whereas primary amide groups react with formaldehyde comparatively readily[94], secondary amides as well as peptide groups do not react with amines and formaldehyde under similar conditions[91,95].

On the basis of indirect data, some workers have also concluded that the methylene bridge is formed via a reaction of the Mannich type when proteins are treated simultaneously with formaldehyde and glycine[97] or other aminoacids[98]. The tanning effect of formaldehyde is mainly associated with similar reactions. It has been shown that, in a mixture with formaldehyde, aminoacids with a longer molecule act as less active tanning agents than glycine[98].

Apart from the free amide or guanidine groups, the NH group of indole is involved in the "cross-linking" reactions[73] (the aminomethylation of the α-carbon atom of indole was mentioned above[77]).

As already mentioned, aminoacids undergo a Mannich type reaction with NH-acid substrates such as amides; a number of studies have been made on reactions of this kind[106-110].

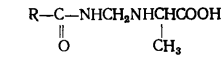
In particular, a number of communications report the synthesis of polymeric Mannich *N*-bases of type (LI) from *N*-hydroxymethylacrylamide, a free aminoacid, and methylenebisacrylamide[107] or from the acrylamide–methylenebisacrylamide copolymer, formaldehyde, and an aminoacid[108]:



(LI)

Here R is a residue of the optically active aminoacid, including L-proline and L-phenylalanine.

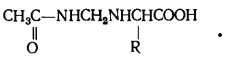
Complexes of polymeric Mannich *N*-bases with copper(II) or nickel(II) salts have been suggested for the resolution of aminoacids into optical isomers[106-108]. The synthesis of alanine derivatives (LII) has been reported[109]:



(LII)

R=CH_3, C_6H_5, 4-$O_2NC_6H_4$, 2-HOC_6H_4, 2,5-$(HO)_2C_6H_3$, or $C_6H_5CH(OH)$.

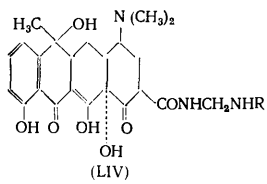
Aminomethyl derivatives of acetamide (LIII) have been obtained by the reaction of the latter with formaldehyde and certain aminoacids, namely valine [R = $CH(CH_3)_2$], norvaline (R = $CH_2CH_2CH_3$), phenylalanine (R = $CH_2C_6H_5$), and α-aminobutyric acid (R = CH_2CH_3)[110]:



(LIII)

Under these conditions, glycine, β-alanine, and α-aminobutyric acid form a mixture of products which has not been separated.

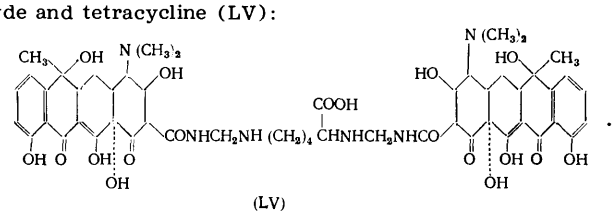
The majority of studies on the aminomethylation of NH-acid compounds have dealt with tetracyclines[14,111-116]. Condensation of aminoacids with formaldehyde and tetracyclines involves the amide group (the Einhorn reaction) with formation of aminomethyl derivatives of tetracycline (LIV):



(LIV)

R=CH_2COOH, CH (CH_3) COOH, CH $(CH_2C_6H_5)$ COOH, CH $[(CH_2)_3NH_2]$ COOH, CH $[CH_2CH(CH_3)_2]$ COOH, CH $[CH(CH_3)CH_2CH_3]$ COOH, CH $[(CH_2)_4NH_2]$ COOH, CH $\left[(CH_2)_3NH{-}C(=NH){-}NH_2\right]$ COOH, CH $(CH_2CH_2SCH_3)$ COOH, or $(CH_2)_nCOOH$ (n=3—10).

The results of the aminomethylation of tetracycline by aminoacids such as glycine, α-alanine, phenylalanine, ornithine, and arginine indicate unambiguously the formation of monoaminomethyltetracyclines (LIV)[111,112]. However, it has been shown for lysine that the condensation involving the second amino-group is also possible[113] and that the bis-derivative (LV) is formed in the presence of an excess of formaldehyde and tetracycline (LV):

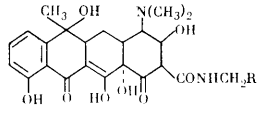


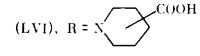
(LV)

The authors[113] emphasise that not more than two formaldehyde molecules react with lysine.

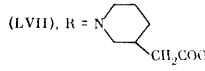
Numerous studies on this problem have now been carried out[99-105].

Among aminomethyl derivatives of tetracycline, compounds (LIV) with R = $(CH_2)_nCOOH$ and n = 3–10 have been obtained in high yields (up to 87–94% for n = 3–5)[114]. A derivative of γ-aminobutyric acid (n = 3) has also been described[115,116]. A synthesis of aminomethyl derivatives of tetracycline (LVI) and (LVII), in which the amino-fragment consists of residues of piperidine-3(4)-carboxylic and piperidine-3-acetic acids, has been proposed[116]:





(LVI), R =



(LVII), R =

IV. AMINOMETHYLATION OF PH-ACID RESIDUES

PH-acid residues—phosphorus and organophosphorus acids and their derivatives—are also used in the condensation reaction with aminoacids and formaldehyde. Like α-aminomethylphosphonic acids[117], *N*-phosphonomethylglycines have been obtained by a reaction of the Mannich type[118–122]. The *N*-phosphonomethylglycines widely used in practice as herbicides are largely obtained by other procedures[123–126].

N-Phosphonomethylglycine (LVIII) has been obtained by the condensation of dialkyl phosphonate [dialkyl halogen phosphite?] with formaldehyde and glycine followed by the hydrolysis of the resulting dialkyl ester of *N*-phosphonomethylglycine (LIX)[118]:

$$(RO)_2P(O)H + CH_2O + H_2NCH_2COOH \xrightarrow{NaOH} \underset{(LIX)}{(RO_2)P(O)CH_2NHCH_2COOH} \xrightarrow{H_2O(H^+)} \underset{(LVIII)}{(HO)_2P(O)CH_2NHCH_2COOH}.$$

The reaction between phosphorous acid, formaldehyde, and glycine taken in proportions of 2:2:1, leads to the formation of *N*,*N*-bis(phosphonomethyl)glycine (LX) (the authors used a different name—*N*-carboxymethyl-*N*,*N*-bismethylphosphonic acid)[119]. In contrast to compound (LIX), obtained at a low temperature in an alkaline medium[118], compound (LX) was synthesised at 110 °C in the presence of hydrochloric acid:

$$2H_3PO_3 + 2CH_2O + H_2NCH_2COOH \xrightarrow{HCl} \underset{(LX)}{HOOC-CH_2N[CH_2P(O)(OH)_2]_2}.$$

The mechanism of the acid dissociation of *N*-carboxymethyl-*N*,*N*-bismethylphosphonic acid has been studied and the structure of its anionic forms has been established[119].

N-Protected glycines condense with phosphorous acid and formaldehyde to form compounds of the type of Mannich bases. Thus *N*-hydroxy-*N*-phosphonomethylglycine (LXI) has been synthesised from *N*-hydroxyglycine[120]:

$$HO-NHCH_2COOH + H_3PO_3 \xrightarrow{CH_2O} \underset{(LXI)}{HOOCCH_2-\underset{\displaystyle OH}{\underset{|}{N}}-CH_2P(O)(OH)_2}.$$

The condensation of the ethyl ester of *N*-benzylglycine takes place analogously. Having removed the benzyl group, *N*-phosphonomethylglycine (LXIII) can be obtained from *N*-benzyl-*N*-phosphonomethylglycine (LXII)[121]:

$$C_6H_5CH_2NHCH_2COOC_2H_5 + CH_2O + H_3PO_3 \xrightarrow{H_2O} \underset{\displaystyle CH_2P(O)(OH)_2}{\underset{|}{C_6H_5CH_2NCH_2COOH}} \xrightarrow{HBr} \underset{(LXIII)}{HOOC-CH_2-NHCH_2P(O)(OH)_2}.$$
(LXII)

Di(carboxymethylaminomethyl)phosphinic acids have also been synthesised by the Mannich reaction[127]:

$$2C_6H_5CH_2NHCH_2COOH + 2CH_2O + H_2P(O)OH \longrightarrow \underset{(LXV)}{\left[HOOC-CH_2-\underset{\displaystyle CH_2C_6H_5}{\underset{|}{N}}-CH_2\right]_2P(O)OH} \longrightarrow \underset{(LXIV)}{[HOOC-CH_2NHCH_2]_2P(O)OH}.$$

Compound (LXIV), obtained by the debenzylation of the condensation product (LXV) with palladium, was converted into various salts.

Using iminodiacetic acid as the amino-component in the Mannich reaction, compound (LXVI) has been obtained by the mechanism[128]

$$CH_3-P(OH)(CH_2-N(CH_2COOH)_2) \xrightarrow[3)\ \text{ion-exchange resin}]{1)\ H_2SO_4,\ 2)\ H_2O_2} \underset{(LXVI)}{CH_3-P(=O)(OH)(CH_2NHCH_2COOH)}.$$

V. BIOLOGICAL PROPERTIES OF MANNICH BASES DERIVED FROM α-AMINOACIDS

It has been shown[81] that many β-aminoketones derived from aminoacids such as glycine, alanine, valine, serine, methionine, leucine, threonine, ethionine, and α-methylmethionine as well as various salts based on the carboxy- and amino-groups exhibit a high bactericidal activity. The broad spectrum of the bactericidal activity (against both gram-positive and gram-negative micro-organisms) as well as their fungicidal activity suggest the possibility of using this group of β-aminoketones in various branches of industry (for example, the textile and paper industries).

The anti-inflammatory and antipyretic properties of *N*-[β-(*p*-substituted benzoyl)ethyl]glycines, alanines, and the ethyl esters of some of them have been investigated[82,83]. Comparison of the antipyretic and anti-inflammatory properties of the hydrochlorides of the ethyl esters of *N*-[β-(*p*-substituted benzoyl)ethyl]glycines[82] showed that the hydrochloride of ethyl *N*-[β-(*p*-isobutoxybenzoyl)ethyl]glycinate, introduced intra-abdominally in a dose of 50 mg kg^{-1}, exhibits an anti-inflammatory and an antipyretic activity. However, these properties of the preparation were not shown after peroral administration in doses of 50, 100, and 200 mg kg^{-1}.[82]

It has been noted that compounds (XXXVI), (XXXVII), and (XXXIX) have a low toxicity.

The influence of β-aminoketones derived from alanine and glycine, compounds (XXXIX) and (XXXVI) with R = Cl or Br, on the coronary blood circulation has also been studied[83]. Among these, only *N*-[β-(*p*-nitrobenzoyl)ethyl]alanine (XXXIX, R = NO_2) exhibits a weak coronary artery expanding activity. Compared with a series of *N*-[β-(*p*-alkoxybenzoyl)ethyl]- and *N*-[β-(*p*-halogenobenzoyl)ethyl]-alanines (XXXIX, R = alkoxy-group, Cl, or Br) shows that the introduction of the nitro-group in the *p*-position in the benzene ring leads to the appearance of vasodilatory activity.

Three compounds of the series of *N*-[β-(*p*-alkoxybenzoyl)-ethyl]glycines with various substituents (XXXVI, R = C_3H_7O, C_4H_9O, or iso-C_4H_9O) have been tested for their anti-tumour activities. The last two compounds exhibit an anti-tumour activity against Erlich adenocarcinoma (53 and 50% suppression of tumour growth respectively has been observed).

Like tetracycline itself, its aminoacid derivatives are of considerable interest as antibacterial agents. In contrast to other antibiotics of the tetracycline group, the aminomethyl

derivatives (*N*-pyrrolidino- and *N*-morpholino-methyltetracyclines, known as reverin and morphocycline) and, particularly, the aminoacid derivatives (glycino- and lysino-methyltetracyclines—glycocycline[13] and lymecycline§) dissolve much more readily in water. Thus lymecycline is 5000 times more soluble than tetracycline[130]. In terms of their antibacterial activity, aminomethyl derivatives are similar to tetracycline[129–132]. Furthermore parenteral administration of lymecycline does not give rise to local secondary responses, frequently observed when tetracycline is administered[14]. Comparison of reverin and glycocycline showed that, while their therapeutic effects (following intravenous administration) are similar, the latter is preferable because of the absence of side effects[131].

As stated above, *N*-phosphonomethylglycines were used as highly effective herbicides[121–126], fungicides, and plant growth regulators[127].

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§ Lymecycline is also known as tetralysal.

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The Interaction of Metals with Proteins

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Various types of interactions in metal-protein systems are examined, the co-ordinate bonds between metals and proteins and their influence on various levels of organisation in protein molecules are specially considered, and examples of practical applications of metal-protein systems are presented.
The bibliography includes 132 references.

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I. INTRODUCTION

There is now a multiplicity of both novel experimental communications as well as reviews concerning various aspects of the interaction of proteins with metal cations (for example, Refs.1–10). However, most of the published studies deal with specific and comparatively narrow aspects of metal–protein interactions. For example, a number of experimental publications exist in the Soviet literature[11–13] reflecting purely structural aspects of the problem, but a distinct deficiency of review publications is felt.

Reitel[14] believes that a protein can be regarded as a system involving interactions characteristic of linear polypeptides containing between 100 and 1000 aminoacid residues. We think that one cannot limit the treatment merely to interactions of polypeptide chains with one another; one must take into account the entire set of interactions of polypeptide chains with one another, with the solvent, and with high-molecular-weight and low-molecular-weight components and the protein must be regarded as polypeptide chains in a system of interactions. One of the significant types of interaction is that with metal cations.

In the present review an attempt is made to follow a combined approach to the consideration of the interaction of proteins with metals against the background of other types of interactions and to assess the role of metals at various levels of the organisation of the protein. This approach has not so far been realised in published reviews; it can promote both a better understanding of the theoretical aspects of the functioning and properties of protein systems and the solution of practical problems which are important for medicine, biology, and biochemistry as well as a new branch of chemical industry—the technology of the isolation and processing of proteins.

II. BIOLOGICAL FUNCTIONS AND TYPES OF INTERACTIONS IN METAL–PROTEIN SYSTEMS

Historically the interest of investigators in metal–protein interactions has been associated primarily with the biological activity of metal ions[15,16]. In 1973 a collected volume of review articles was published under the title "Metal Ions in Biological Systems", in which biological, chemical, and medical aspects of the role of metals *in vivo* are discussed; they include (as a rule in relation to individual specific examples) also the problems of the interaction of metals with proteins (for example, the role of zinc in the functioning of enzymes[19], the importance of vanadium for the vital activity of plants and animals[20], and the role of copper in haemocyanine[21]).

Proteins incorporating a metal in their composition play an important role in biocatalysis and in the metabolism of all living organisms. These proteins have come to be divided into four groups[22,23]: enzymes, redox proteins, transport proteins, and storage proteins. The activity of many enzymes depends on the presence of cofactors, which frequently consist of metal ions; for example, the activities of arginase and carbonic anhydrase depend on the presence of manganese(II) and zinc(II) ions respectively[24].

Table 1. The role of metal ions in biological processes[17].

Metal	Form of location in organism	Strength of binding to protein	Function
Na, K	mobile	low	charge transfer, osmotic equilibrium, transmission of nerve pulse
Mg, Ca	partly mobile	moderate	formation of structures, "trigger" (initiating) reactions, hydrolysis, transfer of phosphate, regulation of cell functions
Mn, Fe Co, Cu, Mo	static	high	catalysis of oxidation-reduction reactions, formation of active centres in enzymes
Zn	static	high	"superacid" catalysts

The group of redox proteins, which are involved in oxidation-reduction processes whereby electrons are transferred in photosynthesis, in the fixation of nitrogen, in mitochondrial respiration, and in the introduction of an oxygen atom into the molecule or in the elimination of a hydride ion, consists of cytochromes and iron- and sulphur-containing proteins (ferredoxin, rubredoxin).[22] Transport proteins—transferrin, ceruloplasmin, iron–porphyrin oxygen-transferring agents (haemoglobin, myoglobin), non-haemin iron-proteins (haemerythrin), and copper-proteins (haemocyanine), and storage proteins (ferritin) regulate the concentration of metals and substrates in the organism, ensuring their presence at the sites where they are needed[25,26].

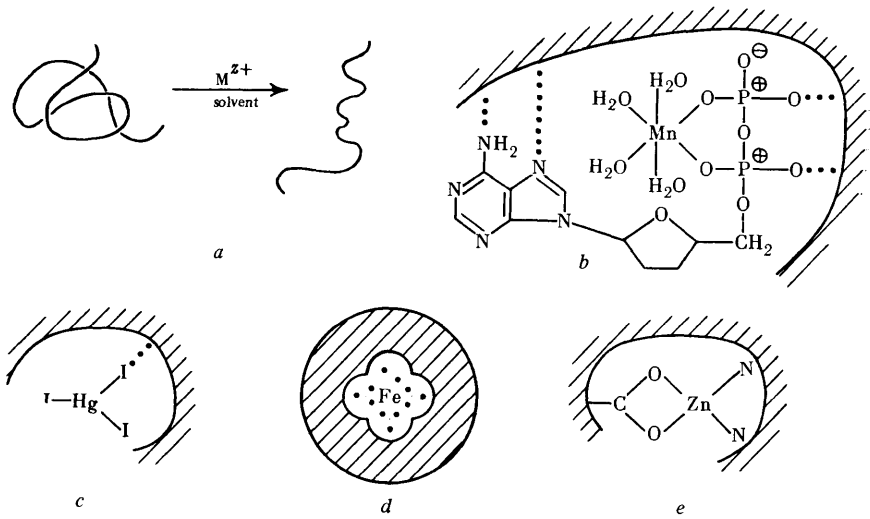


Figure 1. Classification of metal–protein interactions: *a*) indirect interaction via the solvent (lyotropic effect);[27,28] *b*) indirect interaction via an organic ligand[35–37]; *c*) indirect interaction with hydrophobic regions via an inorganic ligand[6,38]; *d*) supermolecular clathrate compounds[39–42]; *e*) coordination interactions with the functional groups of aminoacid residues[19,43].

It is also possible to differentiate a fifth group of metal-proteins—kidney proteins responsible for the binding and elimination of heavy metals from the organism, although so far in the literature they are not combined in a separate class and there is no complete information about their physiological role.

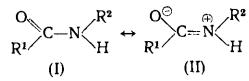
In Table 1 [17] an attempt is made to treat systematically the role of metals in biological processes. Evidently the biological activity of metals is not always determined directly by the strength of their interaction with the protein.

Various types of interactions occurring in metal–protein systems are presented below (Fig. 1). The suggested five types of interactions are fairly conventional and do not exhaust all theoretically possible cases. Nevertheless this scheme, which is not free from internal contradictions, permits a systematic treatment of most of the experimental data available at present.

The first type of interaction—mediated by the solvent—involves the interaction of metal ions and proteins (the lyotropic effect, Fig. 1*a*). Since an aqueous medium is most characteristic of natural systems, we shall consider the influence of metal ions on the protein in such media. The stability of the structure of such protein molecules in solution is usually determined by the hydrogen bonds formed by peptide groups, dipole–dipole interaction of polar groups, and hydrophobic interaction[27,28]. The lyotropic effect of metal ions is of a combined type and includes the following versions: interaction with charged groups, interaction with dipoles (including the peptide bond), and weakening of the hydrogen bond[29].

The interaction of metal salts with charged groups of the protein has a significant influence on the solubility of the latter, since association of the cationic and anionic groups on the surface of the protein with counterions leads to the neutralisation of these groups and weakens the electrostatic attraction between protein molecules. As a result, when salts in low concentrations are added, the solubility of the protein increases.

Proteins contain various readily polarisable functional groups capable of interacting with ions and consisting of dipoles. Most of these dipoles are formed by peptide bonds, which can exist in two *meso*-forms (I) and (II):



(I) (II)

By virtue of the double bond between the carbonyl carbon and the nitrogen in form (II), the rigidity of the structure, necessary for the arrangement of the polypeptide chains in native proteins, is ensured. The addition of metal ions can influence the contribution of mesomeric forms (I) and (II), can weaken the double bond character, and can promote free rotation[30].

Under the influence of metal ions, hydrogen bonds can weaken and even fully rupture if the affinity of the polar group for the ion is comparable to the affinity for its analogue in the hydrogen bond. The rupture of the hydrogen bond, which is an element of the native conformation of the protein, leads to the uncoiling of the peptide chain.

Hydrophobic interactions differ from all other lyophobic interactions by the fact that their energy relations are determined by two factors: firstly, the dispersion forces between the non-polar molecules in contact and, secondly, by the change in the structure of the solvent (water) on interaction with non-polar molecules. Contacts between non-polar molecules and water diminish the entropy as a result of the increase of the fraction of ordered elements in water. The minimisation of such contacts (the transfer of molecules to a non-polar environment or their association) is therefore accompanied by an increase of entropy and a shift of the system to a more favourable energy state[31].

The arrangement of the polypeptide chain in space is such that the hydrophobic aminoacids form the nucleus of the globules, while the hydrophilic aminoacids are distributed on its surface. As a result of electrostatic interaction, the metal ions exert a considerable influence on the structure of

water[32,33], altering the difference between the energies of the water aggregates on the hydrophobic surface of the protein molecule and disturbing the thermodynamic equilibrium in such a way that the aminoacid residue, previously oriented inwards, can become oriented outwards, i.e. the protein molecule with a compact arrangement can uncoil (become denatured). The uncoiling of the molecules results in their aggregation and the reduction of the solubility of the protein. Such increase of the energy of the interaction of protein molecules with one another and the so-called salting out usually occur at high metal salt concentrations in solution[34].

Interactions of the second type are also indirect (via the organic ligand) and occur in bridged complexes (Fig. 1*b*). Such binding is characteristic of many enzymes and transport proteins, including porphyrin-containing proteins[35–37]. In Fig. 1*b* this type of interaction is illustrated schematically for the binding of manganese(II) to creatine kinase via the nucleotide substrate and the formation of a ternary complex: manganese–adenosine diphosphate–creatine kinase[35].

Interactions of the third type are characterised by the addition of heavy metal ions to the protein molecule in hydrophobic pockets (Fig. 1*c*). The addition product is stabilised by van der Waals forces acting between the inorganic readily polarisable ligand and the hydrophobic region of the protein molecule[6,38]. Such addition is characteristic of mercury and gold iodides. In addition, there is a possibility of a direct interaction of certain metal cations with these regions, which is accounted for by the structure of the electron shell of these cations, responsible for their hydrophobic character and the extremely low affinity for water molecules. A high affinity for hydrophobic regions explains the accumulation of Hg^{2+}, Ag^{+}, and Cu^{+} ions in fatty tissues[6].

Interactions of the fourth type involve the formation of supermolecular clathrate compounds formed by storage proteins, a characteristic representative of which is ferritin (Fig. 1*d*). A ferritin species contains 24 identical protein subunits, within which is incorporated an inorganic nucleus approximately 73 Å in diameter containing up to 4500 iron(III) atoms in the form of a basic hydrogen phosphate gel[39–42]: $(FeOOH)_8(FeO{-}OPO_3H_2)$.

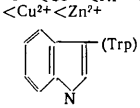
Finally, interactions of the last type, which have been most thoroughly investigated, involve the formation of coordinate bonds between the metal and the functional groups of the aminoacid residues in the polypeptide chain. In Fig. 1*e* these are illustrated schematically for the interaction of zinc with a glutamic acid residue and two histidine residues in the enzyme carboxypeptidase A.[19] Interactions of this type play the most significant role in the structure and functioning of metal–protein systems and must be considered in greatest detail.

III. COORDINATE BONDS BETWEEN METALS AND PROTEINS

Metal complexes with aminoacids and peptides have served for many years as model systems for the investigation of the reactions between metals and proteins. An exhaustive review of the literature up to 1968 was published in 1969;[44] in recent years a multiplicity of novel investigations of new metal complexes with aminoacids and of their practical applications have been published[45,46].

However, despite the extensive literature data, on the basis of results of the binding of metals to aminoacids, it is difficult to draw inferences about metal–protein compounds, since the binding of the metal to the functional groups of the protein differs significantly from its binding to the same groups in small peptides and aminoacids, where the cooperative nature of the interaction of the functional groups, which may have approached one another in the tertiary structure of the protein, is very important. On the other hand, the functional groups in the polypeptide chain are separated by tens of aminoacid residues and act comparatively independently of one another, obeying the geometrical requirements imposed by the structure of the protein. This steric structure can change on coordination of the metal ion, which complicates the study of this process still further. The active centres of enzymes are located as a rule in non-polar pockets within the protein structure where the metal ion is coordinated in fact under the conditions of a non-aqueous medium. Furthermore, the number of coordinating groups in the protein is greater than required to bind the metal, so that the metal ion has a "choice". The protein contains groups with unlike charges which can facilitate or hinder the approach of the cation to the potential ligand without being directly involved in complex formation.

Table 2. Classification of metals and ligands in terms of the HSAB theory[6,47–49].*

Type of compound	Class A (hard)	Intermediate	Class B (soft)
Acids	Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Co^{3+}	$Fe^{2+}<Co^{2+}<Ni^{2+}<Cu^{2+}<Zn^{2+}$	Cu^{+}, Ag^{+}, Hg^{2+}, Pd^{2+}, Pt^{2+}
Bases	H_2O, $RCOO^-$ (Asp, Glu),	 (Trp),	R_2S (Met), RS^- (Cys),
	ROH (Ser, Thr), RNH_2 (Lys, Arg)	$-C_6H_4OH$ (Tyr)	 (His)

*Preferred coordination series: $RCOO^- > RNH_2 > RS^- > H_2O$ in class A and $RS^- > RNH_2 > ROH \gg H_2O$ in class B.

When one comes to consider the probable centres of the interaction of metals with the functional groups of the proteins, one usually begins with the concept of hard and soft acids and bases (HSAB, Table 2).[47–49]. In terms of this concept, all metal ions have acid properties and are divided into hard (class A) and soft (class B). Hard metal ions have a low polarisability as a consequence of their small radii and a high positive charge. They form the most stable complexes with donor atoms which have a high electronegativity, a low polarisability, and small radii and are difficult to oxidise, i.e. with hard bases (for example, N, O, or F). Soft metal ions have a low positive charge and are readily polarised and form the most stable complexes with readily oxidised and polarised ligands—soft bases (for example, S, P, or I). There exist also intermediate acids and bases exhibiting both hard and soft properties depending on the conditions.

In relation to protein systems, hard metal ions endeavour to combine with hydroxy- and carboxy-groups and water molecules. Coordination to sulphur-containing groups and the imidazole residue of histidine is preferred for soft metal ions. Since certain metal ions occupy an intermediate position in this classification, their softness or hardness depends on the bases surrounding them. The arrangement of the metal cations and ligands in the hardness–softness series makes it possible to predict qualitatively the relative strengths of the possible metal–protein coordinate bonds.

Table 3 presents the stability constants of the complexes of certain cations with aminoacids in model experiments and with aminoacid residues in peptides and proteins. Comparison of

the stability constants of metal complexes with aminoacids in Table 3 and the hardness series in Table 2 shows that the majority of cations behave as intermediate species even in the simplest model systems, while the experimental constants for peptide and even more so protein complexes are inconsistent either with the HSAB theory or with the stability constants of the aminoacid complexes. The quantities obtained experimentally in the study of metal–protein equilibria can be referred to as constants only as a matter of convention—the vast majority of the constants published in the literature are stoichiometric quantities calculated for individual complexes within a narrow range of concentrations of both the protein and the cation. The data presented in Tables 4 and 5 show that, in different concentration ranges and at different ionic strengths, different experimental constants can be obtained[57–59].

Table 3. The stability constants of metal complexes of aminoacids ($\lg K$) and aminoacid residues in peptides and proteins ($\lg K'$).*

Aminoacid	Fe^{2+} [51]	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
	lg K					
Glycine	—	7.8	8.9	11.0	15.4	9.3
Aspartic acid	11.4	8.5	10.7	12.7	15.4 [52]	10.4
Glutamic acid	12.1	—	8.1	10.3	14.4 [53]	3.5
Arginine	8.7	—	6.9	9.1	13.8	8.1
Cysteine	—	—	—	—	—	9.9 [55]
Methionine	9.1	—	—	—	—	—
Histidine	4.7	9.3	12.7	15.9	—	12.0
			lgK′			
Cysteine	—	—	—	—	—	7.0 [56]
Histidine	—	—	—	—	3.1—4.4 [54]	2.5 [55]

*Unless otherwise stated, the results were taken from Albert[59].

Note. The numbers in square brackets denote references (Ed.of Translation).

Table 4. The coordination binding of zinc(II) ions to bovine serum albumin.

pH	Medium	t, °C	lg K	References
5—9	0.15 *M* KCl	25	2.9	[57]
6.5	0.2 *M* $NaCH_3COO$	30	3.9	[58]
6.8	0.5 *M* $NaClO_4$	25	9.6	[59]

The scatter of the experimental quantities can be accounted for by many factors. The constant for the binding of a cation by a protein molecule depends on the change of the hardness of the metal in the course of its desolvation and coordination, the changes in the ionic strength of the system, the pH, and the size of the solvation shell, and the conformational changes in the protein. Apart from these factors, account must be taken of the fact that the change in the concentration of the metal ion in a protein solution leads to the binding of the metal at new sites and gives rise to the possibility of oligomerisation or even polymerisation of the protein species, which alters the stability constants. It is at present impossible to take into account all the factors enumerated above in the experimental determination of the binding constant. Thus the determination of the true constant for the binding of the cation to the protein or a specific fragment of the polypeptide chain is very difficult both experimentally and mathematically.

Formally the interaction with the protein can be represented by the equation[6]

$$pM^{z+} + qH^+ + rA^{y-} = M_pH_qA_r^{(zp+q-ry)} ,$$

where p, q, and r are the numbers of metal ions (M^{2+}), protons, and protein molecules (A^{y-}), which form the complex. Here A^{y-} is the base of the polynuclear protein molecule in which all the dissociable protons have been split off.

Despite all the difficulties, significant advances have been made in the quantitative estimates for coordination interactions. As an example, one may quote a study[60] in which the coordination interaction of copper with ribonuclease was considered (Table 5); the sites where copper(II) is coordinated at the functional groups of the aminoacid residues of ribonuclease have been determined exactly.

Table 5. Coordination interaction of copper(II) with ribonuclease[60].

Ligands and their positions in primary structure	Degree of saturation of coordination centre, %		
	pH 5.5; 10^{-5} M $CuCl_2$	pH 5.5; 5 × 10^{-5} M $CuCl_2$	pH 7.0; 3.5 × 10^{-5} M $CuCl_2$
α-NH-R, Lys^{-1}; carboxyl, Lys^{-1}; γ-carboxyl, Glu^{49}; hydroxyl, Ser^{80}	37 ± 4	98 ± 8	24 ± 5
Imidazole, His^{119}; γ-carboxyl, Glu^{111}; H_2O bound to γ-carboxyl, Glu^7	28 ± 4	86 ± 7	33 ± 7
Hydroxyl, Ser^{21}, hydroxyl, Ser^{22}; hydroxyl, Ser^{23}; α-NH-R, Ser^{24}; guanidine, Arg^{39}	27 ± 4	72 ± 11	42 ± 5
Imidazole, His^{105}	14 ± 3	67 ± 8	29 ± 5
γ-Carboxyl, Glu^{86}	13 ± 4	44 ± 8	—
Imidazole, His^{119}, H_2O bound to γ-carboxyl, Asp^{121}	—	—	47 ± 6
Guanidine, Arg^{10}; hydroxyl, Ser^{50}; β-carboxyl, Asp^{53}	6 ± 3	22 ± 7	—

In the study of the interaction of zinc(II) ions with serum albumin (L) various workers observed and demonstrated the existence of several forms of the complex having the general formula Zn_pL_r: ZnL, Zn_2L, Zn_6L_2, $Zn_{16}L_4$ and $Zn_{26}L_6$.[57–59] The formation of $Zn_{16}L_4$ and $Zn_{26}L_6$ is accompanied by the formation of two new bridges comprising zinc(II) ions with a zinc–imidazole binding constant of approximately $10^{3.3}$.

It is of particular interest to note that, although fairly numerous cations can be bound by any protein molecule, there exist certain protein–cation pairs, exhibiting a specific affinity for one another, whose interaction constants, corresponding to certain physicochemical parameters of the medium, are higher by several orders of magnitude than the binding constants for other pairs. This applies primarily to the so-called "metal-dependent" enzymes and the cations participating in the formation of their active centres, for example, zinc(II) in alcohol dehydrogenase[61] and manganese(II) in pyruvate carboxylase[62]. Furthermore, there exist in nature proteins without enzymic activity and having a hitherto unelucidated biological function, which bind selectively certain cations: the Ag-binding protein in rat

liver[63], the Au-binding protein in rat kidneys[64], the Zn-binding factors in rat liver and muscles[65] and in cow's milk[66], and the Cd-binding proteins in the lymph of earthworms[67].

The most probable metal coordination centres in the polypeptide chain are presented in Table 6. The terminal amino-groups (No.1 in Table 6) are the most usual sites for the binding of metals despite their high pK, since the nitrogen atoms of the amino-groups are strongly electron-donating, while the oxygen atoms of the carboxy-group are separated from them by not more than four atoms and can form a chelate ring[50,68]. Coordination to the terminal amino-groups without chelate formation is a much rarer phenomenon and is characteristic of silver and platinum[69,70]. Carboxy-groups (No.2 in Table 6) either participate in chelate formation together with the terminal groups or interact with metals capable of monodentate coordination[19,71,72].

Table 6. Preferred centres for the coordination of metal ions in proteins.

No.	Functional group	Metal	Example of coordination	Refs.
1	Terminal amino-groups	Zn(II), Ag(I), Pt(II)	Pt with α-chymotrypsin	68
2	β,γ-Carboxy-groups (Asp, Glu)	Fe(II), Ag(I), Cu(II), Zn(II), Ca(II), Mn(II)	Zn(II) with Glu residue in carboxypeptidase A	19
	ditto	ditto	Mn with Asp and Glu residues in concanavalin A	69
3	Phenolic OH (Tyr)	—	$(UO_2)^{2+}$ with Tyr residue in tosyl elastase	73
	ditto	—	Fe with Tyr residue in haemerythrin	74
4	Imidazole (His)	Cu(II), Zn(II), Co(II), Fe(II), Ni(II), Cd(II)	Cu(II) with imidazole residue of haemocyanine	75,76
	ditto	ditto	Zn(II) with imidazole residue of insulin	91,23
5	Sulphydryl (Cys)	Ag(I), Hg(II), Mn(II) Fe(II), Co(II), Ni(II), Zn(II), Pb(II), Cu(II)	Cu(II) with Cys residue in "blue" copper-containing proteins	77
	ditto	ditto	Fe with Cys residue in rubredoxin	23
6	Thioester (Met)	Pd(II), Pt(II), Ag(I), Cu(I), Hg(II)	Pt(II) with Met residue in ferricytochrome *c*	80
	ditto	ditto	Cu(II) with Met residue in azurin	23
7	Peptide	Na(I), Ca(II), Co(II), Hg(II), Cu(II), Zn(II), Ni(II), Co(III), Pd(II), Pt(II)	Co(II) and Hg(II) with amide oxygen in biuret	82
	ditto	ditto	Zn(II) with glycylglycine	83

Coordination to metal ions is not very typical for the hydroxy-group of tyrosine (No.3 in Table 6) and the examples in Table 6 [73,74] are perhaps some of the few instances known at the present time. Serine and threonine are more often involved in coordination via the nitrogen atom of the amino-group and the carboxyl oxygen[50,58].

The nitrogen atoms of the imidazole group of histidine are the most important centres for the binding of metals (No.4 in Table 6). The coordination activity of this group can be explained by the fact that the nitrogen of the imidazole groups is an effective electron donor capable of forming stable covalent bonds at the physiological pH.[75,76] The sulphur atoms of methionine, cystine, and cysteine interact preferentially with soft cations (Nos.5 and 6 in Table 6). The sulphur atom is highly polarised in the field of metal ions and is a powerful electron donor. Either monodentate coordination only to the sulphur atom or bidentate complex formation with participation of a nitrogen or oxygen atom in addition to sulphur are usually encountered[77,78,80]. Coordination with participation of a bivalent sulphur atom may be complicated by the oxidation of sulphur to the quadrivalent state and the corresponding reduction of the metal ion[79].

The oxygen of the peptide group (No.7 in Table 6) has weakly basic properties and interacts with metals when chelate formation with participation of a neighbouring amino-group is possible. The oxygen of the peptide group interacts with alkali or alkaline earth metals and this interaction is apparently ionic[81]. The peptide nitrogen binds metals only when the process is accompanied by its deprotonation[84].

IV. THE EFFECT OF METALS ON VARIOUS LEVELS OF THE ORGANISATION OF THE PROTEIN

It may be regarded as firmly established that any local microchemical changes in the protein macromolecule (addition of a low-molecular-weight compound, addition or elimination of the metal, change in the valence of the added metal) [19,29,59,85–96] can lead to significant conformational and configurational rearrangements in the biopolymer. Up to the present time, there is no information about the inclusion in the polypeptide chain of the protein molecule of any fragments other than aminoacids. The question of whether one can assume that the coordination of the functional side groups of the aminoacid and of α-peptide groups to metal cations entails a change in the primary structure is more in the nature of a philosophical-methodological kind and its answer is outside the framework of this review.

The effects of metals on the secondary structure has been most fully studied in relation to collagen[29]. The structural unit of collagen is the cylindrical tropocollagen molecule which consists of three helically intertwined polypeptide chains. The stepwise (with a displacement corresponding to 1/4 of the length) parallel arrangement of the triple helices of tropocollagen ensures the construction of the collagen fibrils. The addition of metal ions to the system can lead either to the stabilisation of the native helical structure of the polypeptide chains of collagen or to their uncoiling and the denaturation of the protein. A series of cations are given below in order of their increasing denaturing effects on collagen[29]:

$$\underset{\text{helix}}{\longleftarrow} \qquad \underset{\text{coil}}{} \qquad WO_4^{2+} < Al^{3+} < NH_4^+ < Rb^+,\ K^+,\ Na^+,\ Cs^+ < Li^+ < Mg^{2+} < Ca^{2+} < Ba^{2+}.$$

The uncoiling of the polypeptide chains of collagen is associated with the increase in the number of groups bearing like charges in the protein under the influence of the metal cations. The repulsion of like charges leads to swelling, an increase in the volume of the molecule, and a rearrangement of the helical chain into a more ordered configuration (coil).

The above series of "dehelicising" activities of cations is valid only in relation to collagen; for other proteins, series of this kind have not yet been set up and may not correspond at all to that illustrated above, particularly since in the organisms of animals (*in vivo*) the coordination of collagen to calcium actually promotes the formation of helices and an increase of the rigidity of the supermolecular formations[85].

The dependence of the catalytic properties of enzymes on the presence of metal cations in solution is a sensitive indicator of the changes in the tertiary structure of the protein. In the case of "metal-independent" enzymes the change in catalytic activity may be caused by the effect of cations,

mediated by the solvent, which induces changes in the physicochemical parameters of the medium. This type of interaction was examined above in Section I. In the case of "metal-dependent" enzymes the change in catalytic activity is associated with configurational changes occurring as a result of the direct coordination of the metal to the protein. The change in configuration and the loss of catalytic activity occur either as a result of the removal of the metal from the active centre, of the competitive replacement of one cation by another, or as a result of the addition of a further metal ion even to one side of the active centre[19].

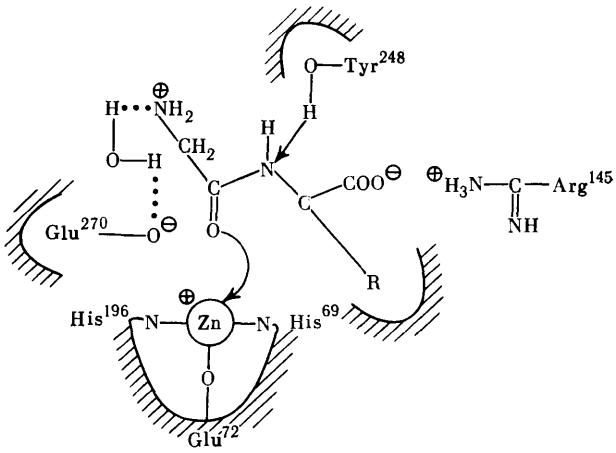


Figure 2. Orientation of the substrate on the surface of carboxypeptidase A.[87]

The optimum catalytic activity, i.e. the existence of the enzyme in the conformational state most favourable for the reaction, is ensured over a comparatively narrow range of concentrations of the added cations. For example, in carboxypeptidase A the Zn^{2+} ion is involved in the orientation of the substrate on the surface of the enzyme molecule (Fig. 2). The removal of the metal leads to a shift of the glutamine (Glu^{270}) and tyrosine residues, subsequent changes in the molecular configuration, and loss of activity[19,86]. An increase of the concentration of the zinc ions in solution is accompanied by the addition of further cations to the enzyme, uncoiling, and polymerisation of the protein molecules via hydrophobic interactions and the formation of salt bridges[59].

In the light of the foregoing considerations, "metal-independent" enzymes strictly speaking do not exist—all enzymes respond to the presence of cations in the system. The only difference is in the concentration of cations giving rise to this effect: Na, K, and Li act indirectly via the solvent and their activity is manifested at high concentrations; Zn, Cd, and Mn, which are coordinated directly to the protein molecule, are active in microamounts.

It is frequently impossible to draw a clear boundary between the changes in the secondary, tertiary, and higher-order structures, since the changes in one of the levels of the organisation of the protein molecule entail the rearrangement of the protein in all its structural levels. This can be well illustrated in relation to the oxygenation of haemoglobin[88,89]. Oxygenation begins with the addition of the O_2 molecule to one of the four haemoglobin sub-units with formation of the O–Fe bond, the iron atom of certain aminoacid residues being displaced from the initial position (Fig. 3). These changes are responsible for further transformations of the tertiary and quaternary structures. After the oxygenation of two sub-units, the molecule as a whole assumes the oxy-configuration, while the two remaining sub-units retain the previous tertiary structure and the latter is now strained, which subsequently facilitates their oxygenation.

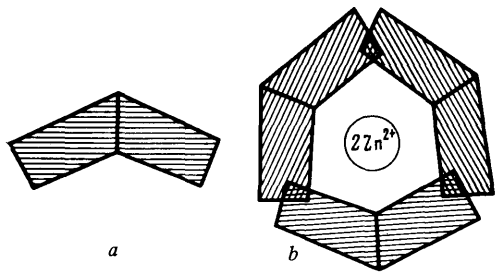


Figure 4. The interaction of insulin with zinc: *a*) dimer; *b*) hexamer.

The change in the quaternary structure has been studied most thoroughly for the interaction of proteins with zinc[90–92]. For example, in the case of insulin, which consists of a dimer comprising two polypeptide chains in solution, the addition of zinc ions results in the formation of a hexamer, in which three dimers are linked to two zinc ions. The coordination

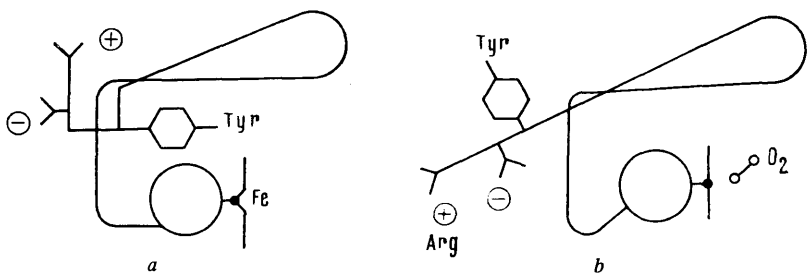


Figure 3. Change in the structure of haemoglobin in the oxygenation process[88]: *a*) deoxy-form; *b*) oxy-form.

of zinc to insulin alters the packing density of the polypeptide chains in the hexamer—they are virtually intertwined with one another (Fig. 4). An increase of the concentrations of the protein and zinc ions in solution increases the size of the aggregates.

In the general case the phenomenon of the aggregation of the protein under the influence of cations is characteristic of solutions of all proteins. The nature of the aggregation depends on the properties and concentration of the protein and the cations. It has been observed[93] that X-ray diffraction by metmyoglobin crystals begins to change when the Zn^{2+} : protein ratio becomes $\geq 3:1$. A further increase of the concentration of zinc ions leads to the disruption of the crystal and the appearance of a brown deposit of the insoluble zinc proteinate. Polymerisation and subsequent precipitation with increase of the concentration of zinc ions have been observed for bovine serum albumin[99]. The interaction of copper(II) ions with insulin also results in the formation of a polymeric protein complex[94].

Table 7. The types of possible steric structures in the aggregation of protein under the influence of cations: $pM^{z+} + rA^{y-} + qH^{+} \rightarrow M_pH_qA_r^{(pz+q-yr)}$.

Type of coordination	Metal	Protein	p	r	Structure
1	Zn^{2+}	Insulin	2	3	soluble species
2	Ca^{2+}, Mn^{2+}, Ni^{2+}	Actin	2	2	fibril formation
3	Ca^{2+}, Mg^{2+}	Casein	3	2	three-dimensional network (gel)
4	Fe^{3+}	Casein	3	1	coagulate
	Zn^{2+}	Metmyoglobin	4	1	coagulate

When actin reacts with calcium, manganese, strontium, and nickel ions, a linear polymer is formed; the interaction with zinc[95] and lanthanum[96] ions leads to non-linear polymerisation. The type of three-dimensional structure produced by the protein as a result of the formation of salt bridges between the protein species is determined by the number of cations which can be bound by the protein species and by the packing density of the species linked by salt bridges (Table 7 and Fig. 5).

When calcium ions are coordinated to actin, each protein species binds not more than two cations and can become aggregated via two salt bridges with not more than two other protein species—aggregates with a linear structure and soluble in water are formed (Table 7, type 2). When calcium ions are coordinated to casein, each casein micelle can bind several ions, which interact with the carboxyl and phosphate groups located on the surface of the caseine micelle. At a protein concentration of 12–15% and a calcuim ion concentration of 0.02–0.1 *N*, a continuous three-dimensional network of protein molecules is formed throughout the volume of the system (Table 7, type 3), which leads to gel formation[97,98]. A decrease of the protein concentration and an increase of the calcium ion concentration lead to closer packing of the protein species, the flocculation of the protein, and the formation of a deposit. Magnesium acts similarly[99]. Iron cations are coordinated to a much greater set of functional groups of the protein molecule than calcium and magnesium, so that the addition of iron to the protein solution gives rise to a closer packing of the protein species owing to a disordered aggregation (Table 7, type 4), which results in precipitation over a wide range of protein and metal concentrations[99].

V. PRACTICAL ASPECTS OF THE APPLICATIONS OF METAL–PROTEIN SYSTEMS

Historically, the practical applications of metal–protein interactions began long before the principal concepts of the chemistry of proteins were formulated. The traditional employment of metal–protein interactions for the conservation of food products and in the leather industry constitute a negligible proportion of the modern applications. Their use is developing most successfully in fields such as biotechnology, the food industry, medicine, and others.

The coordination interaction of polyvalent cations with collagen constitutes the basis of the processes involved in the tanning of leather and furs by aluminium and chromium salts[100–105]. The tanning of collagen-containing material by salts makes it possible to regulate its practically important properties such as resistance to moisture, elasticity, and mechanical strength. Treatment of leather and wool by fluorozirconates[106,107] increases the stability of the material without diminishing its elasticity.

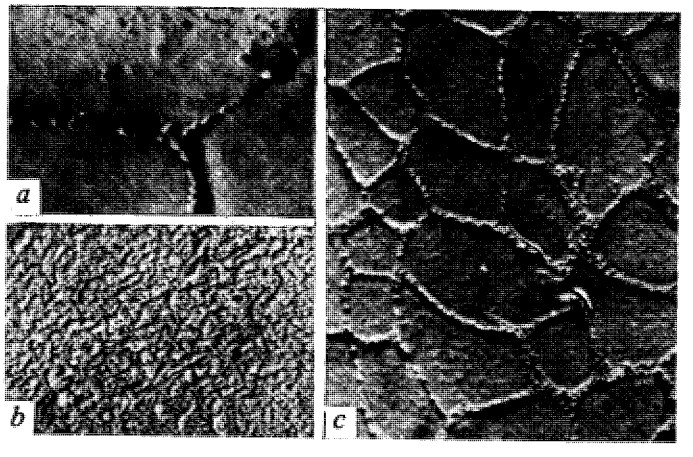


Figure 5. The aggregation of proteins under the influence of metal ions: *a*) fibril-formation; *b*) three-dimensional network (gel); *c*) coagulated material.

Regulation of the solubility of proteins as a result of interaction with salts has found extensive applications in the food industry, in the conversion of isolated protein mixtures into food products. The addition of magnesium and calcium salts to solutions of milk and plant proteins makes it possible to obtain structured systems imitating the fibrous structure of meat products[108,109] and gel-like systems[97,98]. Calcium salts are used to precipitate the lipoprotein complex (the cheese clot) in cheese making[110]. Aluminium salts are used to prepare artificial protein skins for sausages[111] and iron(III) salts serve to increase the mechanical strength of the skins on artificial protein caviare[112,113].

Bivalent and tervalent iron salts are used to precipitate food proteins from very dilute solutions[114–117], which is the most economical method of concentrating and isolating proteins. The converse process is also known—the elimination of heavy metal ions (mercury, copper, lead, tin, etc.) from water by coprecipitation with proteins[118].

Isomorphous complexes of proteins with heavy metals are widely used in electron microscopy[119] and in the X-ray diffraction analysis of proteins[120]. Selective complex formation with certain cations is employed in affinity chromatography for the fractionation and preparative isolation of pure proteins[121,122]. It may be hoped that communications concerning the application of rigorously selective complex formation to the converse problem—the isolation of certain cations from mixtures and dilute solutions—will appear in the immediate future.

Coloured protein complexes of metal cations are used not only for analytical purposes (the biuret reaction with copper salts) [123] but also for the preparation of food dyes (the red colour of the bivalent iron complexes of proteins in the presence of ascorbic acid).[124]

Sodium chloride, which is used traditionally to conserve food products, suppresses the activity of the majority of enzymes at high concentrations. At a certain concentration specific to each enzyme system sodium chloride can activate enzymes. This property has been used in biotechnology for the autolytic processing of the biomass of micro-organisms[125]. Calcium, magnesium, and zinc cations are used to induce the autolysis of micro-organisms[126]. The use of zinc is of greatest interest. The addition of its salts at low concentrations makes it possible to activate selectively enzymes in different groups—for example, one can activate nucleases, leaving proteases in an inactive state[127].

The application of metal–protein interactions in medicine is only just beginning. Quite recently reports have appeared of the detection of antibacterial activity in heavy metal complexes (silver, mercury, and gold) of plant proteins[128]. These studies are extremely promising for the creation of new medicinal preparations with a narrowly specific activity. Peroral administration of the coordination compounds of metal cations and proteins has been suggested for the treatment of disorders caused by the deficiency in the organism of microelements such as zinc, copper, iron, chromium, and manganese[129]. The most promising results have been obtained in the treatment of deficiency of iron[130] and zinc[65].

Supermolecular, colloidal metal–protein compounds, similar to natural clathrate compounds, are also used in medicine. Thus a microdisperse insoluble complex of Fe_3O_4 with serum albumin has been administered intravenously as a special contrasting substance for X-ray studies[131]. Analogous colloidal compounds of CaO and MgO with plant proteins are used to regulate the activity of gastric juice[132].

* * *

Many problems of the structure and functioning of metal–protein systems still await solution. Nevertheless practical necessity requires the employment of metal–protein interactions in various branches of industry, medicine, and science. Each year new applications are being discovered for these systems, while the theoretical problems are still not fully investigated and are hardly likely to be solved in the immediate future.

Most attractive are the prospects for the employment of metal–protein interactions in medicine—for the regulation of enzyme activity and the creation of new drugs with a narrowly specific activity, in metallurgy—for the concentration, isolation, and purification of rare and non-ferrous metals in complex mixtures and dilute solutions (sea water), and in the food industry.

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The Chemical Properties of Singlet Molecular Oxygen and Its Importance in Biological Systems

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Typical chemical reactions of singlet molecular oxygen with organic substances as well as its disruptive influence on biological systems (the photodynamic effect) are described. The involvement of singlet oxygen in carcinogenesis is demonstrated. A new (luminescence) method of detecting singlet oxygen in solution is discussed. The role of singlet molecular oxygen as an oxidant in polluted city air is noted.
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I. CHEMICAL REACTIONS OF SINGLET OXYGEN WITH ORGANIC SUBSTRATES

The oxygen molecule has three possible lowest electronic states which differ in the population of their highest-lying molecular orbitals (Fig.1). The first state ($^3\Sigma$) has the lowest energy, since the two electrons in the highest orbitals are located in different regions of space and consequently their mutual repulsion is minimal. The second state ($^1\Delta$) has a higher energy, since greater interelectron repulsion corresponds to two electrons in the same orbital $\pi^*(2p_y)$. The energy of the third state ($^1\Sigma$) is higher still, since its attainment requires the expenditure of a fairly large amount of energy in order to reverse the spin of the electron in one of the π^* orbitals.

The first state is the ground triplet state and the other two are excited singled states. The singlet states $^1\Delta$ and $^1\Sigma$ lie 22.5 and 37.5 kcal mol^{-1} above the ground state[1]. Singlet molecular oxygen is in general designated by $^1O_2$ in contrast to ordinary oxygen which is designated by $^3O_2$ (or simply by O_2). Fig.1 shows that oxygen in the ground state or "triplet" oxygen has two unpaired electrons; it is a stable biradical of the type $^{\cdot}O-O^{\cdot}$ and its chemical reactions are of the free radical type[2]. As an example, one may quote the radical chain autoxidation of isopropyl alcohol:

$$HOC(Me)_2H \xrightarrow[-\dot{O}_2H]{^3O_2} HO\dot{C}(Me)_2 \xrightarrow{^3O_2} HOC(Me)_2O-O^{\cdot} \xrightarrow[-HO\dot{C}(Me)_2]{HC(Me)_2OH} HOC(Me)_2OOH.$$

It was initially postulated[3-6] that the $^1\Sigma$ state must exhibit a similar reactivity. However, it has been established[7] that the $^1\Sigma$ state relaxes in solution to the $^1\Delta$ state over a period of approximately 10^{-10} s and the authors[8,9] therefore concluded that the reactions of $O_2(^1\Sigma)$ cannot be detected. Additional experimental data, confirming this conclusion, have

been obtained[10]; the author of the above study, who used a wide range of photosensitisers to investigate the reactions of singlet oxygen, established that the proportions of the reaction products do not change when the energy of the triplet state of the sensitiser is below the energy required for the formation of $O_2(^1\Sigma)$. Furthermore, according to the theory $O_2(^1\Sigma)$ cannot undergo concerted addition reactions[11], whereas the reactions of singlet oxygen are concerted[12-14]. We shall therefore consider below only the reactions of the $O_2(^1\Delta)$ form.

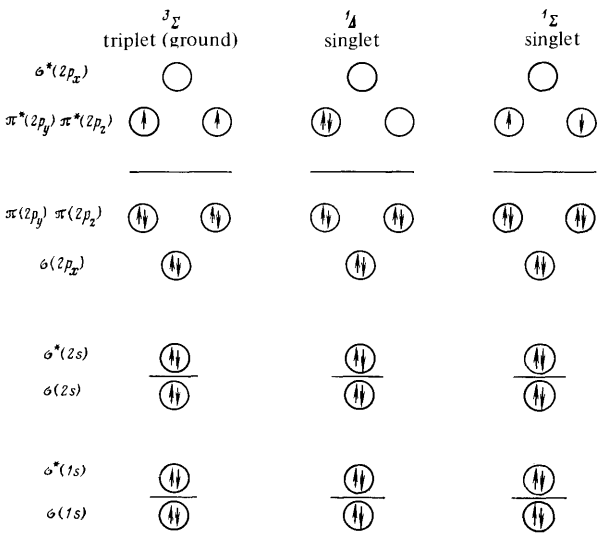
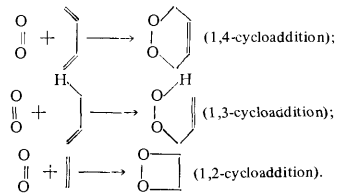


Figure 1. Possible electronic states in the oxygen molecule.

Singlet oxygen in the $^1\Delta$ state is extremely reactive, since, apart from the fact that it has an excess of energy, its lifetime is anomalously long (2700 s in the gas phase at a low pressure and approximately 10^{-5} s in solution).[15,16] The molecule of singlet oxygen in the $^1\Delta$ state can be represented by O=O (Fig.1), i.e. in its electronic structure it resembles ethylene and behaves in reactions as a dienophile[17-19].

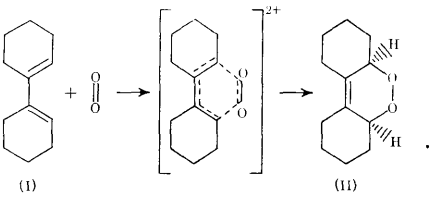
Thus the chemical properties of singlet oxygen in the $^1\Delta$ state are completely different from those of oxygen in the ground state. For example, the characteristic reactions of $O_2(^1\Delta)$ are 1,4-cycloaddition of the Diels–Alder type and 1,3- and 1,2-cycloaddition[11,20-28]:



These three types of reactions give rise to simple methods for the introduction of the peroxy-linkage into organic substrates and are important for the synthesis of new compounds. There is a multiplicity of examples of each type of cycloaddition, only some of which are presented below. More detailed data on the chemistry of singlet oxygen can be found in various reviews[10,11,17,21,22,28-31].

1. 1,4-Cycloaddition (the Endoperoxide Pathway)

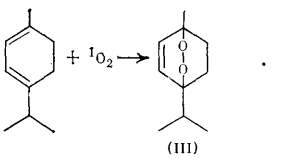
The concerted nature of the reaction involving cycloaddition to dienes has been observed in the addition of oxygen to 1,1'-bicyclohexenyl (I) in the *cis*-conformation. The reaction yields exclusively the *cis*-peroxide (II):[21]



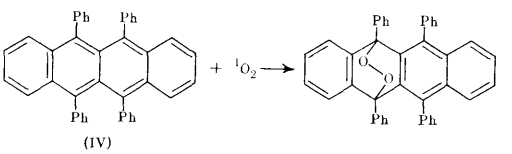
The addition of singlet oxygen proceeds via the formation of a six-membered cyclic transition state, as in the Diels–Alder reaction[10,17].

In the study of the effect of temperature on the rate of reaction of singlet oxygen with a series of dienes, it was found that the activation energy varies from zero for the more reactive dienes to approximately 6 kcal mol^{-1} for comparatively inert dienes[32]. The concerted nature of the reaction and the low activation energy for the addition of singlet oxygen to dienes agree with the theoretical results[11].

Numerous studies have been made on the reactions involving the addition of $^1O_2$ to dienes[21,27]. The *endo*-peroxide (III) (ascaridole) was isolated already in the first half of this century from chenopodium oil and was subsequently found to be formed in plant leaves in the course of the chlorophyll-sensitised oxidation of α-terpinene:[33,34]

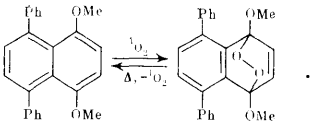


In the laboratory this reaction was discovered in connection with a fundamental study of the photochemical conversion of steroids into vitamin D,[35] where it was shown that ergosterol gives rise to an *endo*-peroxide on oxidation with a dye sensitiser. Extensive studies on the photochemical oxidation of steroid dienes were subsequently carried out[21] and it was observed that aromatic hydrocarbons, for example rubrene (IV), are converted into *endo*-peroxides under similar conditions:[36]



Later numerous studies were made on the photochemical oxidation of polycyclic aromatic and heteroaromatic compounds[21,27,37]. It was found that 9,10-di-substituted anthracenes and polycyclic aromatic compounds which are large molecules react with singlet oxygen almost quantitatively[21,27,37,38]. One should note that, in the photochemical oxidation of hydrocarbons of the acene series, there is no need to employ special sensitiser dyes, since acenes are themselves capable of acting as sensitisers; this also applies to rubrene.

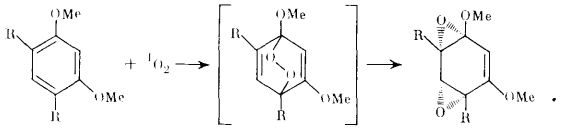
Activated derivatives of naphthalene and benzene also enter into the 1,4-cycloaddition reaction with singlet oxygen; for example, compound (V) can be converted into the *endo*-peroxide (VI):[39]



(V) (VI)

A series of di-, tri-, tetra-, hexa-, and octa-methylnaphthalenes have also been converted into *endo*-peroxides under the influence of $^1O_2$.[40,41]

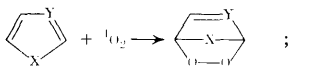
It has been shown that a derivative of resorcinol (VII) is converted into the *endo*-peroxide (VIII) on interaction with $^1O_2$, which results in the formation of the diepoxide (IX):[42]



(VII) (VIII) (IX)

R = t-Bu

A very large series of heterocyclic compounds, particularly five-membered compounds such as furans, thiophens, pyrroles, oxazoles, thiazoles, and imidazoles, undergo the 1,4-cycloaddition reaction with singlet oxygen[21,27]:



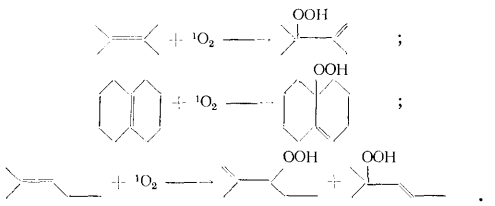
X = O, S, NH, NR; Y = CH, N .

endo-Peroxy-products are unstable and are converted into other compounds or are solvolysed.

2. 1,3-Cycloaddition (the Allylic Hydroperoxide Pathway)

In reactions of this type singlet oxygen adds to olefins, forming allyl hydroperoxides, as in the Alder reaction. The 1,3-cycloaddition mechanism has not so far been established exactly; nevertheless this process is of great synthetic importance, particularly for the series of terpenes, which are the main constituents of various essential oils isolated from flowers, fruits, leaves, and other parts of plants[28]. The reduction of allyl hydroperoxides to allyl alcohols can be achieved on an industrial scale in order to obtain synthetic perfumes.

Numerous studies have been made on 1,3-cycloaddition[10,15,17,22,30,43-49]. Some examples of reactions of this type are presented below:



The experimental observations concerning these reactions can be summarised as follows[11]:

(1) Oxygen is always introduced into the part of the molecule from which hydrogen is removed and the double bond always migrates[10,17,22,29,30,50].

(2) The reaction cannot be inhibited by adding radical trapping agents[50].

(3) For substituted olefins, the ratio of secondary and tertiary hydroperoxides is approximately 1 : 1.[10,17,22,29,30,51]

(4) Groups of substituents which shield the double bond prevent attack by singlet oxygen[52].

(5) There is no loss of optical activity in the oxidation of optically active olefins[50,53]. Furthermore, comparison of the photochemical oxidation reactions of *cis–trans* olefin pairs has shown that *cis–trans* isomerisation does not occur in the course of the reaction[51].

(6) The reactivity of olefins intensifies after the introduction of alkyl substituents (by a factor of approximately 10 per CH_3 group).[19]

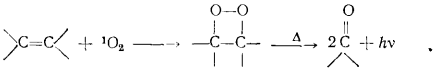
(7) For the majority of olefins, the nature of the solvent has very little influence on the proportions of the products or on the rate of reaction with singlet oxygen[10,17,22,29,30].

(8) There is a satisfactory correlation between the relative rates of reaction of olefins with peracids and with singlet oxygen[19].

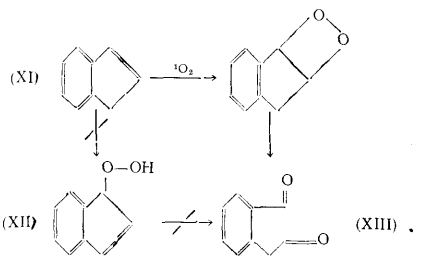
(9) There is a large difference between the rates of reaction of various substituted olefins with singlet oxygen and with free radicals. In the case of singlet oxygen the relative reactivity varies by four orders of magnitude depending on the structure of the olefin, while in the case of trifluoromethyl radicals the variation is only by a factor of two.[19]

3. 1,2-Cycloaddition (The 1,2-Dioxetan Pathway)

One of the most interesting achievements in the chemistry of singlet oxygen has been the discovery of a method for the 1,2-cycloaddition of singlet oxygen to olefins, which leads to the formation of "high energy" 1,2-dioxetans, which emit light and decompose into the corresponding carbonyl products[22]:



The first successful synthesis of a stable dioxetan was reported in 1968.[54,55] This was important, since it had been postulated earlier that carbonyl fragments, which frequently appear in photochemical oxidation reactions, arise as a result of secondary reactions of the unstable allyl hydroperoxides formed initially[17] and not as a result of the cleavage of the intermediate dioxetan. In the same year Foote and Lin[56] and also Huber[57] put forward the hypothesis that dioxetan is one of the three possible intermediates in the reaction of singlet oxygen with enamines. The role of dioxetan as an intermediate in the reactions of singlet oxygen with electron-rich olefins was finally established in a study[58], where it was shown that the dialdehyde (XIII), the only product of the sensitised photochemical oxidation of indene (XI), does not arise as a consequence of the rearrangement of the unstable allyl hydroperoxide (XII):[58]



(XI) (XII) (XIII)

There are many examples of rapid reactions of singlet oxygen with olefins despite the fact that the latter are unable to split off hydrogen atoms in allyl positions[59], which may indicate the formation of dioxetans.

Nitrogen-activated olefins such as enamines, bisacrylidylenes[60,61], indoles[62,63], and dipyrrylmethylenes[64] enter into the 1,2-cycloaddition reaction with $^1O_2$. Alkylthio-substituents are just as effective in activating the ethylene bond with respect to oxidation by singlet oxygen. For example, tetrathioethylenes, which are extremely stable in relation to the usual electrophiles and dienophiles, readily combine with $^1O_2$ to form dioxetans[65,66]. Even monothioethylenes undergo 1,2-cycloaddition[67] rather than attack on the sulphur atom by singlet oxygen[68,69].

II. BIOLOGICAL IMPORTANCE OF SINGLET OXYGEN

1. The Photodynamic Effect

Numerous studies have established[70–79] that virtually all types of biological systems, ranging from the simplest unicellular organisms to multicellular plants and animals, can be damaged by the simultaneous operation of the following three factors: light, oxygen, and a photosensitiser (it is usually a dye); this phenomenon was first discovered in 1900 and was called the photodynamic effect[71,72]. The photodynamic effect can lead to the damage of viruses, fungi, algae, and the simplest unicellular organisms, causing mutations, membrane defects, disturbance of metabolism, etc. (up to the lethal outcome). A number of reviews have been devoted to this effect[70,73–81]†.

The photodynamic effect is based on the photosensitised oxidation of the substrate during which the sensitiser molecule S absorbs a light quantum and passes to an excited singlet state ^1S:

$$S + h\nu \rightarrow {}^1S \quad .$$

From the ^1S state, the sensitiser can pass to an excited triplet state ^3S, which has a lower energy but is longer-lived:

$$^1S \rightarrow {}^3S \quad .$$

This state is in fact involved in the majority of photochemical and photophysical processes. Two main types of reactions of sensitisers in the triplet state have been discovered[17,30]. In reactions of type (I) the sensitiser interacts directly with the substrate, the process involving the abstraction of a hydrogen atom or the transfer of an electron, which leads to the oxidation of the substrate and the reduction of the sensitiser[30]. In reactions of type (II) the triplet sensitiser interacts with oxygen.

According to Kautsky's mechanism[82], which is generally accepted nowadays, the interaction of a sensitiser in the triplet state with oxygen in the ground state involves energy transfer from the sensitiser to oxygen, which results in the formation of singlet oxygen $^1O_2$:

$$^3S + {}^3O_2 \rightarrow S + {}^1O_2 \quad .$$

The singlet oxygen formed then attacks the substrate; in biological systems such substrates are, for example, certain aminoacid residues in proteins, the bases in nucleic acids, and the lipids in membranes. The rate constants for processes of type (I) are $\leq 10^7$ litre mol^{-1} s^{-1}, while those for processes of type (II) are greater by two orders of magnitude and amount to 1×10^9 litre mol^{-1} s^{-1}.[79] In this review only type (II) processes will be considered#. The range of the possible photosensitisers is extremely wide; it consists of dyes (Bengal Pink, Methylene Blue, acridines, etc.), natural pigments (chlorophyll, haematoporphyrin, flavins, etc.), and aromatic hydrocarbons (certain anthracenes, rubrene, etc.). The main condition governing the suitability of the compound as a sensitiser for the reactions considered is that the energy of its triplet state should be not less than 22.5 kcal mol^{-1}, i.e. the energy required for the transition of the oxygen molecule to the singlet state.

It is noteworthy that many medicinal substances such as antibiotics, phenothiazines, and sulphonamides are photosensitisers and can therefore give rise to photodynamic damage in the human organism. For example, it has been observed[84] that the antiobiotics tetracycline, oxytetracycline, and griseofulvin cause a pathological sensitivity of human skin to light.

(a) Protection of organisms against the destructive influence of the photodynamic effect. At the end of the 1960's, it was established that carotenoids can protect organisms against the destructive influence of the photodynamic effect[85]. It was shown on model systems[86] that the oxidation of the substrate by singlet oxygen is effectively inhibited by β-carotene.

The hypothesis that carotenoids can protect photosynthesising systems against the photodynamic effect (when they are sensitised by their own chlorophyll) was put forward as early as 1959 on the basis of experiments with carotenoid-free mutants of photosynthesising bacteria[87]. It was observed that these mutant bacteria are rapidly destroyed in the presence of light and oxygen with sensitisation by their endogenic chlorophyll, while normal bacteria, containing carotenoids, are completely stable under these conditions. Cells without carotenoids, obtained by being grown in the presence of diphenylamine, behave similarly to the carotenoid-free mutant[88].

Experiments on the protecting action of carotenoids have been performed also on animals. Thus haematoporphyrin was administered to mice with and without the addition of β-carotene before exposure to light. It was found that β-carotene affords a significant protection against the photodynamic effect[89].

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† An erroneous lifetime of $O_2(^1\Delta)$ is quoted in the paper of Merzlyak and Sobolev[80] (p.137) (apparently fortuitously); the lifetime of $O_2(^1\Delta)$ generally accepted at the present time is 2700 s (i.e. 45 min).

Bobrovskii and Kholmogorov[83] investigated sensitised photochemical dehydrogenation reactions in model organic systems with the aim of discovering the mechanism of the photodynamic dehydrogenation of the substrates studied (ionol, phenothiazine, and diphenylamine): the question was whether the dehydrogenation is due to singlet molecular oxygen or takes place as a consequence of the direct interaction of the sensitiser in the excited triplet state with the substrate and subsequent dehydrogenation of the reduced sensitiser by oxygen (Santamaria and Prino[84] rule out the electron transfer mechanism because it presupposes the decomposition of the sensitiser, which has not been confirmed experimentally). Tetrapyrrole pigments (chlorophyll, methyl chlorophyllide, phaeophytin, etc.) were used as sensitisers. The authors established that molecular oxygen in the excited singlet state is in fact the active agent responsible for the dehydrogenation of the substrates employed.

These results led to the conclusion that the destructive agent in the photodynamic effect is singlet oxygen and β-carotene protects living organisms against the photodynamic damage by deactivating ("quenching") singlet oxygen. This deactivation takes place via the transfer of the excess energy of excited singlet oxygen to β-carotene, which results in the formation of oxygen in the ground state and β-carotene in the excited triplet state[22,86,90]:

$$^1O_2 + \beta\text{-carotene} \rightarrow O_2 + {}^3\beta\text{-carotene}.$$

Next it was observed that the quenching takes place effectively when carotenes having nine or more conjugated double bonds are used, while quenching by carotenes having seven or fewer double bonds takes place ineffectively or not at all[91].

Another endogenic quenching agent for singlet oxygen is α-tocopherol. The high efficiency of the quenching of $^1O_2$ by α-tocopherol led many investigators to the conclusion that the biological role of this compound consists in protecting the lipid components of biological membranes against oxidation by a singlet oxygen[92–99] (Section II, 1d and II, 3). It was established that there is a correlation between the activity of α-, β-, γ-, and δ-tocopherols as vitamin E and the efficiency of quenching of singlet oxygen by the latter[92,93].

There exist also exogenic quenching agents for singlet oxygen, for example, certain nickel complexes, which are more stable as a function of time than carotenes, since the latter are gradually consumed in the reaction with $^1O_2$.[100] These complexes can be obtained in forms which are soluble either in water or in lipids. 1,4-Diazabicyclo[2,2,2]octane (DABCO) is a very effective quenching agent. However, it was found that this compound is also an effective trapping agent for hydroxy-radicals ($k \cong 2.5 \times 10^9$ mol^{-1} s^{-1}).[101] Sodium azide is also an effective quenching agent, which is readily soluble in water. (For singlet oxygen quenching agents, see also Section II, 3 below.)

Singlet oxygen can be deactivated not only by a quenching agent but also by a chemical trapping agent ($^1O_2$ acceptor); such deactivation gives rise to the corresponding oxidation products in $^1O_2$ cycloaddition reactions. The trapping agent must then satisfy the following criteria[11,102]: a fairly high rate of reaction with $^1O_2$, specificity in relation to $^1O_2$, the absence of complicating side reactions, and ease of analysis of products. Furthermore, the trapping agent must not participate in the generation of $^1O_2$.

Furans are widely used as trapping agents in biology, but, as has been noted by Foote[100], they are not in practice specific, because many othe oxidants, apart from oxygen, oxidise furans to dicarbonyl compounds. Aromatic hydrocarbons giving rise to *endo*-peroxides are more specific[100]. Dimethylcyclohexane gives rise to a characteristic pair of products of interaction with $^1O_2$; it is not very soluble in water, but may be useful in lipid systems[100]. Limonene, which forms six characteristic products of interaction with $^1O_2$, is analogous to the above compound.

According to Foote[100], the best of the probes for $^1O_2$ known at present is the cholesterol system, proposed by Smith and Stroud[102], who concluded that, among the numerous common cell components which might serve as endogenic trapping agents of $^1O_2$ subject to the criteria mentioned above, only unsaturated aliphatic acids and sterols are promising. They showed that cholesterol (cholest-5-en-3β-ol) as well as two other sterols, namely 5α-cholest-7-en-3β-ol and 5α-lanost-8-en-3β-ol, which are present in mammalian tissues, are effective trapping agents for $^1O_2$, satisfying all the criteria enumerated above. The oxidation of sterols by singlet oxygen give rise to hydroperoxides which are completely different from the hydroperoxides obtained in oxidation by normal oxygen (see also Subsections 1c–1e below).

(b) Photodynamic effect on cells and subcellular components. Many types of photodynamic phenomena have been investigated at the cellular level, for example, the loss by the cell of the ability to form colonies, the arrest and anomalies in cell division, the induction of mutations, a decrease of mobility, a change in the permeability of the membrane and in active transport, the loss of ability to maintain the growth of a bacteriophage, etc.[103] These studies were carried out mainly with unicellular organisms such as bacteria[103–108]. In addition, the photodynamic effect has been investigated on cultured mammalian cells. The cessation of growth and destruction of cell enzymes[109], the cessation of mitosis[110], and destruction of cells[111] were observed. There have been reports of damage to cell organelles, but most of the damage is in the nucleus. Many of the mutagenic and lethal effects investigated, manifested in the presence of photo-sensitisers, are due to conformational changes and the breakdown of strands or the destruction of bases in nucleic acids[112].

Depending on which sensitiser participates in the photodynamic effect, the inactivation of the cell can be of three types[113]: (1) when the cell is attacked from the outside and the sensitiser remains outside the limits of the cell; (2) when the cell is attacked from the inside and the sensitiser is located mainly in the cytoplasm; (3) when the cell is attacked from the inside and the sensitiser is bound preferentially to DNA. In these types of inactivation the sites of damage are respectively the cell surface, the cytoplasm (enzymes, RNA, and other subcellular structures), and DNA. An example of a sensitiser of the first type is provided by the dye Toluidine Blue; many thiazine dyes also belong to this category. The second type consists of xanthenes. Acridine dyes, which can cause genetic changes, belong to the third type.

(c) Genetic effects. The photodynamic effect on biological systems in many instances causes damage to genetic material, resulting in mutation or destruction of the system[112]. Genetic effects (more precisely mutations and chromosomal aberrations) have been observed in many biological systems—from viruses and bacteriophages to higher plants and organisms[112,114–118]. The study of the photodynamic inactivation of bacteriophages has shown that the nucleic acid of the bacteriophage is the target for $^1O_2$:[115,116] it was found that guanine is mainly decomposed[117].

The penetration of the sensitiser (dye) into nucleic acid and its attachment are the necessary stages in this effect[118]. Certain acridine dyes, for example, Acridine Orange, are of special interest in the study of the photodynamic mutagenesis in micro-organisms, viruses, and bacteriophages in view of their high affinity for DNA [119] and the ability of being incorporated between neighbouring bases in the DNA helix.[120]

Before the dye is able to exhibit a sensitising effect, it must initially penetrate through the pellicle of the virus. Incubation with a dye in the dark increases the subsequent effect in the light; consequently the penetration of the dye takes place over an appreciable period[112]. It has been shown[121] that only a dye bound within the virus particle is effective. It has also been demonstrated[118] that the molecules of dyes ineffective in inactivating the bacteriophage can also be bound to the active sites of the nucleic acid. When mixtures of effective and ineffective dyes are used, competition for binding by the ineffective dye lowers the degree of inactivation caused by the effective dye[112].

On photodynamic treatment of DNA, many physiochemical changes in its molecule take place in addition to the selective degradation of guanine. The decomposition of DNA after extensive photodynamic treatment using Acridine Orange has been reported[122]. The authors of this study observed a decrease of the melting point of DNA, which indicates

changes in its conformations. They noted that the decrease of the melting point is proportional to the guanine content in the DNA. A decrease of the thermal stability of the DNA of the T4 phage has been observed[117]; the heat-denatured DNA then underwent photochemical oxidation more readily than the native DNA.

The damage to the skeleton of the DNA molecule on treatment has been investigated[123] by noting the changes in viscosity. The authors[123] suggest that the degradation of neighbouring guanine residues leads to the weakening of the bonds in the DNS skeleton.

(d) Photodynamic damage of membranes. The ability of $^1O_2$ to react with lipids has been confirmed in a number of studies[124–128]. The damage to membranes is believed to be caused by the oxidation of lipids as a result of the photodynamic effect[70,73–80]. It has been shown that aliphatic acid derivatives[129] and cholesterol[130] give rise to photochemical oxidation products in which the double bond has been appreciably displaced towards the allylic position, i.e. the interaction of $^1O_2$ with lipids is a 1,3-cycloaddition with formation of hydroperoxides. The rate of reaction of $^1O_2$ with unsaturated aliphatic acids is approximately 1.5×10^3 times higher than for oxygen in the ground state. The non-conjugated hydroperoxides formed in this reaction indicate the involvement of $^1O_2$ in the peroxide oxidation[102,131,132].

The photochemical oxidation of cholesterol in erythrocytes in the hereditary disease "erythropotic protoporphyria" is a particularly important instance of the peroxide oxidation of lipids by singlet oxygen[94,133]. In this disease 10–100 times more protoporphyrin is observed in the erythrocytes of the patients than under normal conditions. Being an effective sensitiser, protoporphyrin produces singlet oxygen, which damages the erythrocyte membranes. Irradiation of the blood of patients suffering from erythropoetic protoporphyria in the presence of oxygen leads to haemolysis. Singlet oxygen then interacts with the erythrocyte cholesterol, forming cholesteryl hydroperoxide, which induces further haemolysis of the erythrocytes[94,133,134]. It has been observed that internal administration of β-carotene constitutes an extremely effective treatment of this disease[135]. α-Tocopherol also exhibits a protective effect in photohaemolysis[94].

(e) Photodynamic effect on proteins. The first communication about the photodynamic effect on proteins appeared as early as 1903.[136] It was shown that enzymes such as diastase, invertase, and pepsin are inactivated in the light in the presence of eosin. Since then numerous investigations of the photodynamic degradation of proteins, particularly enzymes, have been made[76,77,137]. In all the instances studied the photodynamic damage to the proteins is manifested by a change in the side chains of the aminoacids, but there is no dissociation of peptide or disulphide bonds[76,138].

Of the twenty aminoacids encountered in typical proteins, only five are sensitive to singlet oxygen: histidine, tryptophan, methionine, tyrosine, and cysteine, the first three reacting with $^1O_2$ particularly rapidly[139,140]. The aminoacid residues incorporated in proteins are usually oxidised photochemically more slowly than the same aminoacids in a free state in solution. The incorporation of an aminoacid even in a small peptide can alter profoundly its sensitivity to photochemical oxidation as well as the chemistry of the process[77].

Photodynamic treatment entails a series of physicochemical transformations of proteins as a result of a change in the sensitive aminoacid residues. Changes in solubility[141], surface tension[142], viscosity[143], polarographic behaviour[144], diffusion properties[145], light scattering properties[146], the type of sedimentation[147], optical rotation[147], capacity for assimilation under the influence of proteases[148], binding to metals[149] and coenzymes[150], binding to haem[151], etc. have been noted. The majority of enzymes lose their catalytic activity as a result of photodynamic treatment[76,137], hormones lose their activity[149,152], antigenic properties disappear[137], and the reactivity of antibodies is lost[153].

The aminoacid residues sensitive to photodynamic oxidation change at different rates depending on the reaction conditions and on the protein in which they are incorporated. Thus it is possible to carry out the selective photochemical oxidation of only one type of residue or of a series of residues in proteins using specific sensitisers or reaction conditions. Histidine residues in proteins are known to be sensitive to photochemical oxidation only when the imidazole ring of histidine carries no charge[77]. Thus histidine residues are hardly oxidised photochemically at low pH.[76] Consequently at high pH there is a possibility of the selective oxidation of histidine residues, while at low pH other residues can be oxidised[153–155]. The photochemical oxidation of methionine or histidine forming part of the active centre can be used to investigate the mechanism of enzyme action[156].

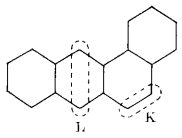
Photochemical oxidation has been used in the conformational analysis of proteins[156–158]. By virtue of the three-dimensional structure of the protein, the residues located on its surface are photo-oxidised at a higher rate than those located at different depths within the molecule. It has been established that the rate constants for the photochemical oxidation of histidine and methionine residues on the surface of the protein are 14 times higher than for those located in the bulk of the molecule[159].

If the sensitiser is associated with the protein, a very high degree of selectivity of the photochemical oxidation of aminoacid residues, located in close proximity to one another as a result of the three-dimensional folding of the protein molecule, is ensured. Chromophores can be bound covalently to specific sites in the protein molecule where they can sensitise the photochemical oxidation of sensitive neighbouring residues. Certain proteins can contain chromophores which are capable of sensitising the photochemical oxidation of aminoacid residues nearby. The required proximity of the sensitiser in the residue depends on the photochemical oxidation mechanism. The photodynamic effect then depends on the distance over which singlet oxygen can diffuse in the course of its lifetime[77]. It has been noted[113] that the possibility of different sites for the generation of $^1O_2$ and for its attack is a unique property of singlet oxygen in the photodynamic effect. Thus the migration of $^1O_2$ through a layer of stearate up to 500 Å thick has been demonstrated[160]. The $^1O_2$ molecule can therefore transport electronic energy over fairly long distances[113].

2. The Involvement of Singlet Oxygen in Carcinogenesis

Numerous attempts have been made to find a correlation between the carcinogenic activity of a compound and molecular electronic factors: charge density[161], electron affinity[162], the ability to form charge-transfer complexes[163], the ability to fluoresce[164], and the energy of the lowest triplet state[165]. The correlation proposed by Schmidt[161] and expressed quantitatively by Pullman and Pullman[166] proved to be best. Pullman and Pullman[166] calculated the charge densities for different carcinogens and observed that carcinogenic activity is

related to the charge density in the K and L regions in polycyclic hydrocarbons:



The K region corresponds to addition to two neighbouring carbon atoms, while the L region corresponds to addition to carbon atoms located in the *para*-positions in the ring. The ease of electrophilic addition in the K and L regions is determined by the charge density at the atoms indicated. The K region can be the site of attachment of the hydrocarbon molecule to the components of the cell[167]. It has been shown experimentally that 1,2 : 5,6-dibenzoanthracene is fixed on the protein of the skin precisely via the K region[168].

It has been demonstrated that the L region of polycyclic hydrocarbons could also be involved in binding to the cell protein[168].

On the basis of the discovery that singlet oxygen can be generated on quenching the excited states of organic molecules (sensitisers) by ordinary molecular oxygen[82,169–171] and bearing in mind the properties of $^1O_2$ as an effective oxidant[12], Khan and Kasha[172] proposed a mechanism of carcinogenesis involving the intermediate participation of singlet oxygen.

According to the model of Pullman and Pullman[166], the two necessary conditions for the carcinogenic properties of polycyclic hydrocarbons are the presence of an active K region and the absence of an active L region. On the basis of their calculations, Pullman and Pullman predicted, for example, the carcinogenic activity of 3,4 : 9,10-dibenzopyrene before this was demonstrated experimentally[173]. Pullman and Pullman were forced to introduce very complex indices into their model in order to account for many experimental observations; nevertheless complete success in predicting carcinogenic activity was not achieved. For example, contrary to the model, 2',3' : 3,4 : naphthopyrene is carcinogenic[172], despite the presence of a very active L region.

According to the theory of Khan and Kasha[172], the initiation of photocarcinogenesis requires that the molecule of the bound polycyclic hydrocarbon should continue to absorb natural sunlight. This type of hydrocarbon molecule, altered as a result of binding to the cell (i.e. the part of the molecule remaining after binding—see Fig. 2), has been called[172] the "optical residue". Thus the bound hydrocarbon molecule plays in this model the role of a bound sensitiser generating singlet oxygen. This mechanism of carcinogenic activity can be represented schematically as follows.

(1) Preliminary binding of the hydrocarbon molecule M to a specific component of the cell Q:

$$^1M + Q \rightarrow {}^1M{-}Q \quad .$$

(2) The excitation by light of the molecule formed:

$$^1M{-}Q \xrightarrow{h\nu} {}^1M^*{-}Q \quad .$$

(3) Intersystem crossing to the triplet state:

$$^1M^*{-}Q \rightarrow {}^3M^*{-}Q \quad .$$

(4) Photosensitised formation of singlet oxygen:

$$^3O_2 + {}^3M^*{-}Q \rightarrow {}^1M{-}Q + {}^1O_2 \quad .$$

(5) The reaction of singlet oxygen with DNA bases initiating the carcinogenic process.

In this model there must be a satisfactory rate of intersystem crossing of the residual molecule from the singlet excited to the triplet state and the energies of the electronic states of the residual molecule must be favourable for the photosensitised formation of singlet oxygen (i.e. the energy of the triplet state of the residual molecule must be $\gg$22.5 kcal mole^{-1}).

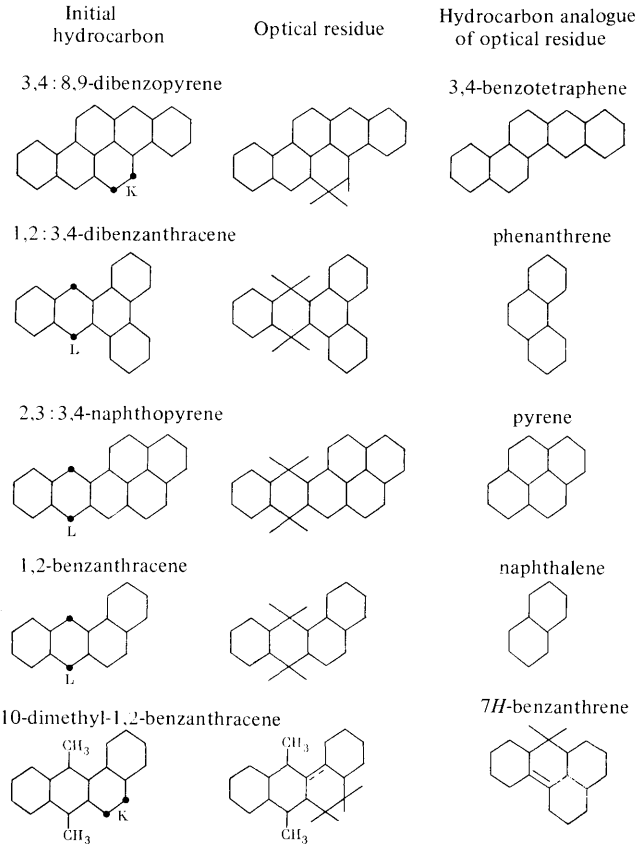


Figure 2. Schematic representation of the optical residues and their hydrocarbon analogues for certain polycyclic hydrocarbons.

Table 1. The absorption of polycyclic hydrocarbons and the analogues of their optical residues after covalent addition to the K or L region[172].

Initial hydrocarbon	λ, nm	Analogue of optical residue	λ, nm
3,4 : 8,9-Dibenzopyrene	480	3,4-Benzotetraphene	410
1,2 : 3,4-Dibenzanthracene	375	Phenanthrene	350
2,3 : 3,4-Naphthopyrene	480	Pyrene	375
1,2-Benzanthracene	390	Naphthalene	317
9,10-Dimethyl-1,2-benzanthracene	390	7*H*-Benzanthrene	350

Khan and Kasha stated that the attachment of the molecule M to the residual cell components via the K or L region shifts two ρ,π orbitals away from the delocalised π-electron system of the polycyclic hydrocarbon molecule as a result of which the optical excitation of the bound molecule requires a higher energy (Table 1), i.e. a blue shift should be observed in the

absorption spectra. The addition via the L region leads as a rule to a more pronounced blue shift of the absorption bands compared with the addition via the K region. This can explain why the presence of an active K region usually favours carcinogenesis, while an active L region normally prevents it. It is noteworthy that the presence of an active L region in the model[172] does not guarantee the absence of carcinogenic activity. Khan and Kasha do not attribute any preferred role to the K or L regions in the induction of cancer; in their model the difference between these regions is determined solely by the optical properties of the residual hydrocarbon from the standpoint of the possibility of the sensitisation of the formation of singlet oxygen.

For example, according to Pullman and Pullman, 3,4 : 8,9-dibenzopyrene (Fig. 2) is a powerful carcinogen, since it has an active K region and has no active L region. Khan and Kasha suggest that the molecule has a carcinogenic activity on the grounds of its optical behaviour, since its addition to a cell component gives rise to an optical residue capable of absorbing sunlight (Table 1). Experimental tests revealed that 3,4 : 8,9-dibenzopyrene is indeed an active carcinogen[172].

The molecule of 1,2 : 3,4-dibenzoanthracene (Fig. 2) has only an active L region and according to the model of Pullman and Pullman should not be carcinogenic. Since addition should displace the absorption spectra to the ultraviolet, Khan and Kasha predicted an insignificant photocarcinogenic activity of this molecule and confirmed this experimentally[172].

The 2′,3′ : 3,4-naphthopyrene molecule (Fig. 2) has no active K region but has a highly active L region and, according to the model for Pullman and Pullman, should not exhibit carcinogenic activity. However, it has been shown experimentally[173] that this compound is a powerful carcinogen. According to the Khan–Kasha model, the residual molecule formed after the addition of the initial molecule via the L region exhibits an optical absorption in the region corresponding to the solar spectrum (Table 1) and for this reason 2′,3′ : 3,4-naphthopyrene should exhibit carcinogenic activity.

Substitution can induce the appearance of carcinogenic activity in molecules which were previously inactive. For example, 1,2-benzoanthracene (Fig. 2) is non-carcinogenic, since the most likely site of the addition of its molecule to the cell component is in the 9,10-positions of the anthracene moiety; such addition shifts the absorption spectrum of the residual molecule to an energically inaccessible region (Table 1). However, the addition of substituents in the 9,10-positions (9,10-dimethyl-1,2-benzoanthracene—Fig. 2) results in the addition of the molecule via the K region rather than the L region and the residual hydrocarbon absorbs sunlight (Table 1). Indeed, 9,10-dimethyl-1,2-benzoanthracene exhibits carcinogenic activity[174].

It is of interest that these planar molecules of polycyclic hydrocarbons—both carcinogenic and non-carcinogenic—are incorporated in DNA molecules[175,176]. Khan and Kasha therefore suggest that the long-lived form of singlet oxygen generated by the residual polycyclic hydrocarbon can diffuse causing oxidation in a very remote section of the DNA chain or can add to certain specific enzyme sites in the cell.

The first experimental test of the theory of photocarcinogenic properties of Khan and Kasha was carried out by its authors[172]. Mice from two colonies (the C_3H breed resistant to cancer of the skin) were smeared with a dilute acetone solution of 3,4-benzopyrene in the standard procedure of the carcinogenic test and were left alone for 5½ months, one colony being placed in a dark room. Twice as many skin tumours appeared in mice living in the normally illuminated room compared with those in the dark room. Control animals living in the dark and normally illuminated rooms did not exhibit this effect.

On the basis of the foregoing, one can conclude that the molecules which are believed to be non-carcinogenic under daylight illumination (the usual wavelength range of solar radiation) can become carcinogenic on irradiation with ultraviolet light.

3. Luminescence in Biological Systems. A New Method of Detecting Singlet Oxygen in a Condensed Phase

Vladimirov[177] began in 1958 studies on ultraviolet luminescence in biological systems; measurements were made with the aid of a photomultiplier cooled with liquid nitrogen and working in the photon counter regime. In 1961 extensive investigations were initiated on the ultraweak glow of tissues and homogenates as well as the glow appearing on oxidation of aliphatic acids (see, for example, Tarusov and Veselovskii[178]).

Among these studies, reactions associated with the action of hydrogen peroxide on biological substrates are especially interesting. An ultraweak glow accompanying the enzymatic decomposition of hydrogen peroxide by catalase, peroxidase, liver homogenates, and yeast and erythrocyte suspensions was observed; the luminescence spectrum was in the range 420–530 nm with maxima at 460 and 510 nm.[177,179] Somewhat later Kachanova and Purmal'[180] confirmed these results, having observed chemiluminescence in the decomposition of H_2O_2 by catalase and metal–amine complexes serving as models of catalase; the emission maximum was observed at approximately 510–520 nm.

In 1966 it was reported[181] that singlet oxygen is formed in the decomposition of hydrogen peroxide by catalase. However, it is claimed[79,182] that singlet oxygen constitutes not more than 0.5% of the entire oxygen formed in this reaction under these conditions. Nevertheless, one can apparently assume that the emission of singlet oxygen is involved in the ultraweak glow occurring in the decomposition of hydrogen peroxide indicated above. The observed region of the $^1O_2$ spectrum includes an emission band at 478 nm, corresponding to the dimolecular transmission[7]:

$$O_2(^1\Delta) + O_2(^1\Sigma) \rightarrow 2O_2(^3\Sigma) + h\nu \quad .$$

Singlet oxygen can then also behave as an intermediate transmitting its excitation energy to other fluorescent molecules[183,184] and can thus participate in luminescence indirectly. There exists yet another mechanism of luminescence involving singlet oxygen. As stated above, $^1O_2$ 1,2-cycloaddition reactions result in the formation of dioxetans, which then decompose into carbonyl-containing fragments, approximately 15% of the fragment molecules being formed in the excited state[185]. This excitation energy can be emitted directly by the fragment or transferred from the latter to a fluorescing molecule[79].

Unfortunately the photomultipliers used to detect the ultraweak glow of plant and animal tissues are insensitive to radiation at wavelengths in excess of 650 nm,[178] while the most characteristic and most intense band in the spectrum of singlet oxygen is at 1270 nm;[11,31,169–171,186] this band corresponds to the $O_2(^1\Delta) \rightarrow O_2(^3\Sigma)$ transition.

The 1270 nm band has been detected by a number of workers in the study of gas-phase systems in the quenching of triplet states of organic compounds by molecular oxygen[11,31,169–171,187,188]. However, in solution it could not be detected for a long time because the lifetime of singlet oxygen in the condensed phase is reduced by eight orders of magnitude compared with the gas phase[7,15,16,184,189,190]. This luminescence band was detected in 1976 by Krasnovskii, Jr.,[191] in air-saturated solutions of various photosensitiser pigments

generating singlet oxygen. The above study[191] was followed by a whole series of investigations by the same author[192–199] who used a sensitive photoelectric technique and solvents (CCl_4, CS_2, and Freon-112) which interact comparatively weakly with $^1O_2$. Aromatic hydrocarbons (anthracene and naphthacene), porphyrins, chlorophylls, bacteriochlorophylls, and phaeophytins were used as photosensitiser pigments. It was found that the spectral region of the flow is independent of the nature of the solvents and pigments.

In all cases a maximum was observed at 1271 ± 1 nm; the emission half-width in spectra recorded using narrow slits (~4 nm) was 18 ± 1 nm, i.e. the glow corresponds to the $^1\Delta$ state of O_2. The luminescence excitation spectra coincided in all cases with the absorption spectra of the photosensitiser pigments. According to Krasnovskii's measurements[192–194], the lifetime of $^1O_2$ in carbon tetrachloride is 28 000 μs, which greatly exceeds the values obtained previously by other workers[202].

Using Krasnovskii's method, it was found that the $^1O_2$ luminescence can be observed in virtually all organic solvents[203] and also in D_2O and H_2O.[195] It is noteworthy that the luminescence quantum yield in D_2O is 400 times smaller than in CCl_4 and amounts to approximately 1.2×10^{-7} and measurement of the $^1O_2$ luminescence in H_2O involves considerable difficulty and a distinct emission maximum could not be observed in H_2O; however, this maximum has been observed largely on diluting D_2O with ordinary water up to the 1 : 1 ratio.

In the study of the above systems Krasnovskii concluded that two processes compete in solutions: photosensitised generation of $^1O_2$ and its quenching in collisions with non-excited sensitiser molecules[192]. He showed that porphyrins, their complexes with zinc, magnesium, and cadmium, chlorophylls, phaeophytins, and retinals effectively generate singlet oxygen[191–198]. Krasnovskii used the quenching of the $^1O_2$ luminescence as a method for investigating the reactivity of $^1O_2$ with respect to various compounds. This method is undoubtedly more accurate than the chemical methods employed hitherto and based on measurements of the rate of consumption of $^1O_2$ trapping agents introduced into the system investigated.

In the course of these experiments it was observed that porphyrins, chlorophylls, and phaeophytins are also effective quenching agents[192–198]. Metal complexes of porphyrins proved to be still more effective quenching agents than metal-free porphyrins; the activity of the quenching agent depends on the nature of the central metal atom and on the structure of the porphyrin ligand. In terms of their activity in the quenching processes, the metals can be arranged in the following sequence:

$$Cu^{2+} < Zn^{2+} < Cd^{2+} \leqslant Mg^{2+} < Fe^{3+} \simeq$$

Porphyrin complexes with Fe^{3+}, Ni^{2+}, and Co^{2+} proved to be the most effective. The quenching rate constant k_q for these compounds are independent of the nature of the ligands and in all cases approach the rate constant for a diffusion-limited process (k_d).

In order to elucidate the quenching mechanism, Krasnovskii measured the rate constants (k_{ox}) for the chemical reaction between $^1O_2$ and quenching agents, which lead to the decomposition of the latter[194,197]. It was found that $k_{ox} \ll k_q$ for porphyrins, chlorophylls, and carotenoids, i.e. the quenching is determined by the physical energy transfer process without the destruction of the quenching agent. For lipids and naphthacene (an aromatic hydrocarbon), $k_{ox} \cong k_q$, i.e. quenching is also determined by the degradative process. On the basis of a comparison of these data, Krasnovskii put forward the hypothesis that two mechanisms of physical quenching are most probable; either direct energy transfer from $^1O_2$ to low-lying levels of the quenching agents or rapid electron exchange in the exciplex between $^1O_2$ and the quenching agents. The first mechanism is possible for quenching agents having energy levels at ≲1 eV (for example, for carotene, bacteriochlorins, and cobalt, nickel, and iron complexes of porphyrins). The second mechanism is more probable for quenching agents without such levels.

The fact that retinals, chlorophylls, and porphyrins are able to generate and quench $^1O_2$ is extremely important for the understanding of photobiological processes such as photosynthesis and vision[197,199]. It is known that the photoreceptors of the retina always contain free retinal which has been shown[197,199] to be an effective photogenerator of single oxygen and can therefore be the cause of the damage of the retina by light. It has been suggested that in the system protecting photoreceptors from singlet oxygen the leading role is assumed by α-tocopherol,[204] whose content in the outer segments of the rods in the retina is 5–10 times higher than in the other biomembranes.

Somewhat later than Krasnovskii's investigations, Khan and Kasha also detected the $^1O_2$ luminescence at 1270 and 1580 nm in liquid solutions[200,201]. They used an extremely sensitive infrared spectrometer with a thermal electrically cooled PbS detector. A much weaker band at 1580 nm corresponds to the $^1\Delta(v' = 0) \rightarrow {}^3\Sigma(v'' = 1)$ transition. $^1O_2$ was generated via photosensitisation of the solution and also chemically in the reaction of hydrogen peroxide with sodium hypochlorite. Benzophenone, haematoporphyrin, etc. were used as the sensitisers, while the solvents were perfluorohexane, Freon, CCl_4, and water.

The $^1O_2$ photoluminescence can be used to detect the ability of various substances to generate $^1O_2$ photochemically and also to estimate the efficiency of this generation process. Thus this new method of detecting singlet oxygen can be very important not only for the study of natural biological processes but also for the investigation of the effect on natural systems of exogenic components, which is associated particularly with problems involving the care of public health.

III. SINGLET OXYGEN IN POLLUTED CITY AIR

The possibility that singlet oxygen plays a decisive role in the formation of photochemical smog in the lower atmosphere was first examined in the 1960's.[205,206] Later this problem was studied in greater detail[207–209]. As a result of prolonged studies of the mechanisms of the formation and decomposition of photochemical smog, Pitts and coworkers[210,211] concluded that singlet oxygen $O_2(^1\Delta)$ and (or) $O_2(^1\Sigma)$ in polluted city air participates in chemical processes as an oxidant. These authors suggested that certain hitherto inexplicable atmospheric chemical and possibly biological effects could be attributed to singlet oxygen.

The ways in which singlet oxygen is formed in polluted city air are examined below. Five mechanisms, explaining the formation of singlet molecular oxygen in polluted city air have been proposed[207]. The first four mechanisms as well as the contribution of each to the production of singlet oxygen are illustrated in Table 2.

1. Direct Absorption of Sunlight

After a series of experiments on a mixture of air and tetramethylethylene in an apparatus with a long optical path, Pitts and Coomber[207,208] concluded that the direct absorption

of visible radiation in the range 550–770 nm by normal oxygen leads to the formation of singlet oxygen $O_2(^1\Sigma)$ (the $^3\Sigma + {}^1\Sigma$ transition at 762 nm), which is rapidly deactivated to the $^1\Delta$ state. $O_2(^1\Delta)$ then reacts with tetramethylethylene and the corresponding hydroperoxide is formed. Furthermore, the absorption at 1270 nm leads to the formation of $O_2(^1\Delta)$. However, since these transitions are formally forbidden, the contribution of this mechanism to the overall production of singlet oxygen in the atmosphere is very small.

Table 2. The formation of $^1O_2$ in polluted city air[220].

Source of $^1O_2$	w^*, 10^{-8} h^{-1}
Direct optical absorption	$<9.2\cdot10^{-3}$
Photosensitisation	80
$O_3+h\nu\rightarrow{}^1O_2+O$ *	0.1
$NO+O_3\rightarrow NO_2^*+{}^1O_2$	1140

*Here w is the rate of production of $^1O_2$.

2. Energy Transfer from Organic Molecules in the Triplet State to Oxygen in the Normal State (Photosensitisation)

A considerable amount of singlet oxygen is obtained by the direct transfer of electronic energy to the oxygen molecule from the molecules of an organic pollutant in the triplet state[207,210,212]. This mechanism is identical with Kautsky's mechanism of laboratory photosensitised oxidation reactions[82]. Spectroscopic studies by a number of workers showed that $O_2(^1\Delta)$ is produced by the gas-phase energy transfer to oxygen from irradiated gaseous aromatic hydrocarbons with (π,π^*)-triplet states (for example, benzene and naphthalene)[169,171,213] and carbonyl compounds with (n,π^*)-triplet states, for example benzaldehyde[208,214]. Energy transfer has also been observed for heterogeneous gas–solid and gas–liquid systems[215].

3. The Photolysis of Ozone

When ozone is irradiated with ultraviolet light, it undergoes photodissociation to an electronically excited oxygen atom $O(^1D)$ and an oxygen molecule in the singlet state[216,217]:

$$O_3 + h\nu_{260\ nm} \rightarrow O(^1D) + O_2(^1\Delta \text{ or } {}^1\Sigma) \quad .$$

This mechanism is particularly important in the upper layers of the atmosphere[218]. In the lower layers it is less important than the energy transfer mechanism[219,220].

A significant consequence of the formation of $O(^1D)$ atoms in this reaction is its involvement in the subsequent energy transfer process:

$$O(^1D) + O_2 \rightarrow O_2(^1\Sigma) + O(^3P) \quad .$$

This results in the formation of two oxidising species; singlet molecular oxygen and atomic oxygen in the ground state[207].

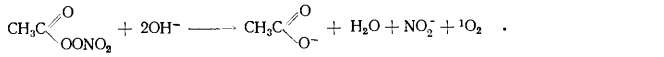
4. Exothermic Chemical Reactions

An important exothermic reaction in a polluted atmosphere giving rise to $^1O_2$ is that between nitric oxide and ozone[207], the rate constant for which is $k = 1.2 \times 10^7$ litre mol^{-1} s^{-1}:[221]

$$NO + O_3 \rightarrow NO_2^* + {}^1O_2 \quad .$$

Furthermore, it has been suggested[222,223] that ozone might react similarly with a series of other substances polluting the atmosphere, such as sulphides, with formation of singlet oxygen. It is known that similar processes in the condensed phase do lead to the formation of singlet oxygen[207].

The high reactivity of peroxyacetyl nitrate (PAN) in chemical and biological systems *in vitro* and *in vivo* is known. It has been shown that PAN is one of the main causes of the irritation of the eyes and the damage to plants by polluted city air[224–226]. Studies on simpler systems have shown that PAN can act both as an oxidising and an acetylating agent[227,228]. Alkaline hydrolysis of this compound leads to the formation of singlet molecular oxygen[207,229,230]:



Thus singlet oxygen must be regarded not only as a possible oxidant acting on the environment but also as an intermediate in the oxidation process.

5. Charge-Transfer Complexes between a Hydrocarbon and Oxygen

Coomber and coworkers[208,209] proposed a fifth way leading to the formation of singlet molecular oxygen, which is as follows. When ultraviolet light is absorbed by short-lived olefin–oxygen or aromatic hydrocarbon–oxygen collision complexes, charge-transfer complexes are formed between the electronically excited hydrocarbon (electron donor) and oxygen (electron acceptor) in the ground state. These complexes can then decompose, giving rise to singlet oxygen and the triplet hydrocarbon[207–209].

When a charge-transfer complex is formed between a hydrocarbon and oxygen, an additional intense absorption band, corresponding to charge transfer, appears in the absorption spectrum of the hydrocarbon, which results in an increase of the intensity of the long-wavelength edge of the hydrocarbon absorption band and in addition the band undergoes a shift towards longer wavelengths ("red shift") (see, for example, Tsubomura and Mulliken[231] and Shinkarenko[232]). The fact that the long-wavelength edge of the absorption band of hydrocarbons becomes more intense and undergoes a bathochromic shift in the presence of oxygen under illumination is extremely important for atmospheric photochemistry. It was believed previously that the presence of many of the polluting compounds in the environment is unimportant because they do not absorb light in the region corresponding to the solar spectrum. However, the red shift of the absorption band suggests that some of these compounds do indeed absorb in the visible region and therefore participate in the photochemistry of polluted city air.

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Structure of Polymeric Carbon

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Experimental results and model ideas on the structural organisation of different forms of condensed carbon are critically reviewed from the standpoint of polymer science. Stress is laid on the role of chemical bonds between molecules (branching points) and of lamellar and other supermolecular formations in the multi-step process leading to a three-dimensional development of the polymeric carbon structure. Many crystalline forms of carbon (in addition to diamond and graphite) are shown to exist as regular polymers of the carbyne or transitional types. 297 references.

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I. INTRODUCTION

Existing views on the molecular and supermolecular organisation of condensed carbon are not universally held. Different schools of workers apply different treatments to their experimental results, and unfortunately even the terminology varies as between laboratories. Published papers contain a profusion of suggested models of the structure of carbonaceous materials which are often mutually incompatible.

Although the original tentative classifications of solid carbon as a type of polymer were soon followed by extensive articles and monographs, the development of the structural physics of carbon lags at least 25 years behind the present level of polymer science. The structure of the various three-dimensionally cross-linked carbon polymers is still largely unexplained, even in broad terms: even the nature of the interatomic C–C bonds, i.e. the structural chemistry of these materials, is far from clear. Typical of this state of affairs are the various coals, carbynes, and carbon thin films. This is true also of the more highly organised carbonaceous materials such as blacks, cokes, graphites, coals, vitreous carbon, pyrolytic carbon, carbyne, schungite, anthracite, diamond, carbon fibres, microporous adsorbents, composite materials, etc. There is hardly any concept in the materials science of carbon which could not benefit from critical re-examination. Our knowledge is still largely empirical, and much more work is needed before a theoretical understanding can be achieved. The problems lie in many different areas of technology. The present period of detailed studies of the properties of different types of polymeric carbon, aiming to establish a large fund of varied experimental data, must now be followed by a period of constructive thought and generalisation. The most urgent need in the physical chemistry of carbon at present is to generalise and unify the existing information.

All structural methods comprise two basically different aspects: the mathematical formalism, with its system of axioms, and the interpretation needed to apply it to specific problems. The two aspects must be carefully distinguished before the structural method can be successfully applied to structurally indefinite and varied materials such as the different forms of polymeric carbon. Unless this is done we cannot be sure that the conclusions from an experiment stem from the theoretical basis of the method rather than from the far more indeterminate interpretation rules.

In setting up the theoretical basis of a method we should avoid, if possible, terms already loaded with connotations, such as crystallite, phase, graphitisation, interplanar spacing, amorphous carbon, defect, and so on. The mathematical results should preferably be formulated in a neutral language, in order to avoid pre-conceived interpretation. The general theory should be, as far as possible, independent of *a priori* assumptions as to the structure of the unknown system. The initial postulates should be clearly stated, they should have the greatest possible generality, and they should not be biassed towards a specific model of the material under study.

A common mistake in the analysis and interpretation of experimental information is to tackle prematurely the most difficult and interesting question: the selection of a suitable working model. The alternative (and more cautious) approach, adopted in this review, concentrates initially on a pragmatic and inductive study of the model.

II. COORDINATION CHEMISTRY OF CARBON. LENGTH OF C–C BONDS

We have a fairly unambiguous criterion for deciding whether or not a chemical bond exists between two carbon atoms, i.e. whether the two atoms belong to the same molecule: the distance (r) between their nuclei. When an interatomic bond is present, r(C–C) = 120–170 pm.[1–3] Distances shorter than 120 pm between carbon atoms are inadmissible, owing to mutual repulsion. The range 120–170 pm, called the "valence bond" region, is followed by a "forbidden gap", from 170 to 280 pm, beyond which comes another band of allowed carbon–carbon distances: r(C–C) > 280 pm. This is the intermolecular interaction band.

The term molecule applies, in principle, to any sub-assembly of atoms in which each atom is chemically bound to one or more atoms of the same sub-assembly[4]. From this point of view a diamond crystal is a single three-dimensionally cross-linked giant macromolecule. Similarly, an atomic layer in an ideal graphite crystal is a single two-dimensionally cross-linked polymeric macromolecule.

According to the modern structural chemistry of carbon a C atom can be chemically bound to two, three, or four nearest neighbours (not necessarily equidistant from it). Stoichev's rule, well known in the stereochemistry of organic compounds, relates the length of the C–C bond to the number of bonds or atoms attached to this bond:

$$r(\text{C—C}) = 129.9 + 4.0\,n \text{ (pm)}.$$

In this expression $n = 2–6$ is the sum of the coordination numbers of the two carbon atoms forming the bond, less 2:

$$n = z_1 + z_2 - 2\,.$$

Other coordination numbers such as $z = 0$ (clathrate bond), $z = 1$ (end-atom in a radical), and $z > 4$ (e.g. in carborane-like fragments), though possible in principle, are not typical of polymeric carbon.

The coordination chemistry of carbon is still far from being fully developed: the chemical behaviour of a carbon atom is usually described in terms of its valence states (sp, sp^2, sp^3 hybridisation of hydrogen-like wave functions). However, a recent review[3] has shown that the coordination number can be used to reveal new facets of the changes in interatomic C–C distance. Thus, though coordination numbers greater than 4 are not normally considered in the structural chemistry of polymeric carbon[1,2,5,6], it is now well established[3] that in carboranes the C atom can have coordination numbers of 4, 5, and 6, so that

$$r(\text{C—C}) = 107.4 + 5.8\,n \text{ (pm)}; \quad n = 6, 8, 9, 10.$$

The longest C–C bond experimentally found in carboranes[3] is 171 pm.

III. COPOLYMERIC NATURE OF CONDENSED CARBON

The term polymeric has been used[7] exclusively for non-graphitising carbon. However, this usage is terminologically incorrect: it would be more exact to treat the concepts of "condensed" and "polymeric" states of carbon as synonymous.

Polymeric (or, more strictly, copolymeric) carbon is an open lattice or network of atomically cross-linked chains (one-dimensional), tapes (two-dimensional), and diamond-like, polyhedral (carborane) fragments, i.e. three-dimensionally linked rod-like, lamellar, and globular fragments. They form[8] a fairly rigid and oriented three-dimensionally cross-linked structure penetrated from all directions by a system of pores which can be open or closed, in the shape of cylinders or disks, lens-like, needle-like, or spherical. Coal has been likened[9–11] to a conglomerate of linear, branching, and cross-connected amorphous polymers, interlinked by intermolecular interaction forces. It is impossible, in general, to identify individual molecules or pores: this explains the failure of various attempts[12–14] to describe the structure of solid condensed carbons and coals in molecular terms (the "small molecule" theory[15]).

The impossibility of describing solid carbon as a molecular substance (like water, benzene, etc.) is now well recognised[16–21]. Thus, according to Biryukov[22], most of the constituents of natural forms of carbon can be classified as high-molecular compounds (HMC). Coals are mixtures of different HMC, with a three-dimensional heteropolycondensed (hydroaromatic) structure and a low level of polycondensation (2–5 rings). The aromatic rings contain substituents in the form of radicals or aliphatic groups. The number of these substituents decreases as the degree of metamorphism of the coal increases. The rings can be interconnected (cross-linked) by methylene bridges, ether bridges, or bridges of the alicyclic, heterocyclic or biphenyl type.

It has been said[9] that the description of coal as a high-molecular compound with a three-dimensional structure destroys the relevance of studies of its molecular structure, since the concept of "a macromolecule" is now known to be physically meaningless in the chemistry of HMC. Nevertheless a clearer knowledge of the individual molecular constituents (segments, fragments, branches) between the branching or cross-linking points is not useful but essential to a better understanding of the organisation of carbonaceous materials.

IV. THE PACKET AND FRINGE MODEL

The most characteristic X-ray diffraction feature of carbonaceous substances is a set of several more or less diffuse maxima corresponding to the graphite structure superimposed on a continuous background. The most important is the first reflexion, in the region of scattering angles (2θ) between 18 and 32° (for $\lambda = 154$ pm), corresponding to the Bragg periods $d = 280–500$ pm. The reflexion is found in various forms in almost any form of carbon, and it is always the strongest. It is usually ascribed to the presence of small crystallites of graphite[23,24], and the spacing d is interpreted as the distance between plane-parallel layers of carbon atoms or aromatic molecules. It is assumed that carbon atoms have a strong tendency for two-dimensional condensation to give aromatic molecules (graphitisation).

The presence of 2–4 diffuse reflexions in positions close to those from the (002), (100,101), (004), and (110) graphite planes has been quoted[25] as evidence that the basic structural unit in coals is the graphite network. However, it is now becoming clear that this assertion is misleading, and that the "coincidence" of reflexions from "amorphous" carbons (coal, schungite, vitreous carbon, carbon blacks, etc.) and from crystalline graphite is in many ways fortuitous[26]. Nevertheless, Warren's turbostratic model[23] of two-dimensionally ordered structures has been increasingly applied to amorphous carbons. The size of the graphite blocks (condensed "aromatic macromolecules") and their mutual orientations were inferred from the width of the reflexion and from the approximate "interplanar spacings". The aromatic model was extended to all forms of carbon, including those which yield a different (non-graphitic) diffraction pattern.

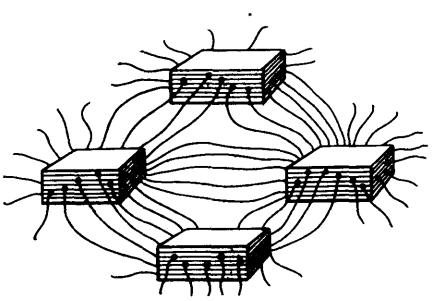


Figure 1. The packet and fringe model of the structure of polymeric carbon.

It is claimed[27] that the presence of graphitic reflexions is direct evidence of the formation of blocks (clusters, packets) of two-dimensional layers of aromatic molecules. On this

evidence the presence of "crystallites" (graphite-like particles, or micelles) having fairly sharp boundaries and immersed in an amorphous matrix has been postulated (Fig. 1). In this model the carbonaceous material is treated as a two-phase system (even without allowing for the presence of pores[27]).

All forms of carbon can be arbitrarily classified into two types[16-20,28-34]: 1) organised (ordered, aromatic, nucleated, crystalline, contained in crystallites) and 2) not organised (amorphous, non-aromatic, peripheral, disordered, lying between crystallites in the amorphous matrix).

The position of the reflexions was assumed to be determined by the internal layer structure of the crystallites, and their width by the external dimensions of the crystallites. The crystallite size was treated as the most important of the structural characteristics, and in most cases it was found to be 1–100 nm. The background continuum of the diffraction picture was ascribed to the amorphous matrix. Several structural models of carbon were proposed, all of them based on an aromatic macromolecule (or layer) surrounded by aliphatic, hydroaromatic, and other atomic groups. The basic structural transformation during carbonisation and heat treatment was assumed (*a priori*) to be the growth and ordering of aromatic macromolecules and crystallites as a result of the rearrangement of atomic groupings with bonds of different types. This approach led to the structural model of carbon which we can call the packet (or micelle) and fringe model by analogy with the now superseded fringed micelle model in the structural physics of linear polymers[35,36].

In this model (the "spider" model) the primary structural fragments were thought to be: 1) a two-dimensional aromatic layer in the crystallite, usually assumed to be planar, i.e. absolutely rigid, and 2) a carbon chain with side-groups of hetero-atoms interconnecting the crystallites.

The bundle of chains terminating on any one crystallite is treated as its fringe[37]. The block (or packet, crystallite, micelle, cluster) is a secondary, supermolecular formation in which the distance between the plane parallel carbon layers varies between 335.4 and 344 pm depending on the degree of correlation (three-dimensional order) in the mutual arrangement of these formations. The lower limit was identified with the ideal graphite structure, and the upper limit with the turbostratic structure, i.e. with a fully uncorrelated disposition of the layers[23,24,30]. However, Ruland has shown[38] that even the spacing d = 344 pm implies some degree of correlation in the disposition of the layers. Thus one of Franklin's fundamental assumptions[30] appears to be incorrect.

The packet and fringe (micelle and fringe, or crystallite) model of the carbon structure was proposed independently in the early 1950's by Franklin[29-32] and by Kasatochkin[16-19,33], and was subsequently developed by many workers[5,14,20,27,34,38-51]. The model has been used to interpret all types of experimental result[1,2,37]: even a method of determining the fractional amount of aromatic carbon was based on it[52]. Numerous models of the disorder (or partial amorphousness) of polymeric carbon have been proposed[23,24,50-57]: in most cases the amorphousness was ascribed to disordered translation, rotation, and bending of the layers[24,58-68], non-identical valence bonds in some of the atoms (Pauling's quinoid structure[63-65]) or non-identical states of the different surfaces of the same (or of different) two-dimensional aromatic molecules[50,51], or to the presence of two phases in the system (the crystallite packet phase + the amorphous fringe carbon phase). It was suggested[5,20,37] that the amorphous carbon can display every possible level of hybridisation of the states of the four outer electrons in each C atom. In spite of the emphasis on a more or less regular packing of the aromatic layers in the packet (or crystallite), the presence of some regularly packed chain-like fragments was implicitly accepted. No other way of interpreting the mass of experimental facts could be found, especially those derived from X-ray diffraction measurements.

However, the position of the first reflexion often corresponds to d > 344 pm,[42-49] and this cannot be explained within the framework of the packet and fringe model[66,67]. Furthermore the intensities of some of the reflexions, in particular the (002) and (004), are often anomalous and do not correspond to the graphite structure[66]. Also, the presence of coherent scattering regions of finite size does not in itself imply that the system must be two-phased, or micro-heterogeneous, as has been recognised in the case of chain (linear) polymers[68,69].

Indeed, high-resolution (~0.3 nm) electron microscopy, interference microscopy (to reveal the periodicity of atomic layers), and phase contrast methods[70] have all been unsuccessful in the search for discrete crystallite particles[67,71-88]. It was found that the size of the bent, twisted, and tangled bundle (micro-fibril), consisting of several tape-like layers (or molecules), can greatly exceed the normal values of L_a and L_c, reaching several micrometres[71-73,81-86]. The finding that not only individual layers (tapes) but also bundles (micro-fibrils) are quite pliable was most unexpected[71-77,87].

The conclusion was that the basic microstructural units include large, distorted graphite layers and long narrow ribbons rather than small three-dimensional crystallites (as suggested by the original X-ray diffraction experiments). Polymeric (rigid, non-graphitising) forms of carbon have been described[7] as a highly distorted form of graphite consisting of tapes rather than layers.

The adherents to the crystallite (micellar fringe) model have now started to describe the crystallite as an assembly of approximately parallel layers without identifiable boundaries between the crystallite and its surroundings, rather than as a normal particle (or micelle)[34,42,66,74-76]. This treatment stems from the belief that the intensity of the reflexion is a measure of defect concentration rather than of the size of the "scattering particle". However, these stipulations amount to admitting the failure of the micellar fringe model of the carbon structure.

V. THE MOLECULAR-TAPE FELT MODEL

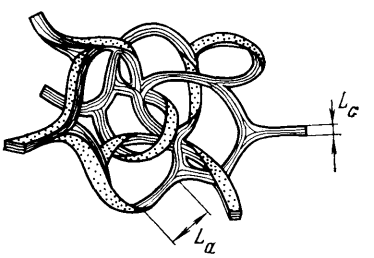


Figure 2. The molecular tape carbon felt model.

The micellar fringe model was followed by the tangled tape model[74,75], in which any carbonaceous substance (from vitreous carbon[72-76] to carbon fibre[7,34,81-88]) is held to consist of a uniform molecular-tape felt without any discrete

supermolecular formations (Fig.2). In this case the difference between vitreous carbon and carbon fibre lies only in the degree of preferred macroscopic (visible) orientation of the ribbon bundles as they diverge, intersect, and come together again[7,44,67].

This model of the structure of carbon was quickly adopted in many published papers and text-books[27,66,89,90]. Nevertheless, in spite of its apparently firm experimental foundations, the model is incompatible with physical reality in two respects. Firstly, by postulating that all the carbon atoms are trigonal (in an exclusively sp^2 hybrid valence state[42]) the felted tape model ignores the possible existence of carbon chains, diamond-like regions with tetrahedral bonds, chemical cross-links, sharp bends, and the intermingling and spiralisation (twisting) of chains, tapes, and layers. Secondly, while rejecting crystallites as real structural elements[73,91], this model also rejects every other discrete structural unit having a higher (supermolecular) level of organisation.

Evidently, in real systems the organisation of the carbon must be less uniform than this model suggests, both from the chemical point of view (interatomic bonds) and from a higher-level standpoint. Recent extensive structural investigations have demonstrated the formation of ordered structures at both the molecular and the supermolecular level not only in crystalline but also in amorphous carbonaceous materials. The formation of these structures is responsible for the loss of three-dimensional homogeneity in carbonaceous materials: it is accompanied by the appearance of interfacial boundaries and localised non-uniformities such as cracks, graphitised regions, and local concentrations of low-molecular compounds.

Johnson and coworkers[92] have proposed a complex model of the fish-scale structure of a high-molecular carbon fibre (HTT† = 3100 K), including intersecting (even at right angles) and longitudinal bundles of aromatic tapes, pores with sharp angles, regions of imperfect packing of the tapes, sharp bends, and twists in the tapes.

Numerous variants of the two basic structural models (the packet and fringe and the felted molecular tape model) of condensed (copolymeric) carbon are described in recent monographs[7,12,15,20,22,27,66,73,90] and reviews[6,8,40–42,48,51,56,89,93]. In principle they do not contradict, but they complement each other, and therefore all can claim some validity. Each variant focusses attention on certain aspects of the structural hierarchy and of the amorphousness of carbon, while other aspects are ignored. In reality the structure of polymeric carbon is infinitely more rich and varied than even the most complex model suggests.

VI. DIRECT EXPERIMENTAL OBSERVATIONS OF THE NON-UNIFORM MOLECULAR STRUCTURE OF POLYMERIC CARBON.

It is widely assumed that all non-crystalline forms of carbon consist of graphitoids: localised packets of aromatic two-dimensional macromolecules. However, in many cases the shapes of the observed diffraction peaks are not described satisfactorily by this model. For example, even Franklin[31] met this difficulty in a study of the carbonisation products of poly(vinylidene chloride) (PVDC) at 1300 K. From an analysis of the X-ray reflexion profiles [mainly of (110) index] Franklin concluded that 65% of the carbon atoms in this material are accommodated in highly perfect, flat graphitic layers, and 35% in an amorphous phase which gives diffuse scattering. Other workers also reported similar observations[14,40,41].

Kirda and coworkers[57] have shown that the average length of the C–C bonds in anthracite, calculated from the position of the first peak on the atomic radial distribution curves, decreases from 145 to 128 pm if the sample is ground for 20 min in a vibro-mill. They concluded[57] that 66.5% of the carbon in the initial sample exists as flat graphitic layers ~2 nm in diameter, and 33.5% can be classified as amorphous, i.e. not organised in ordered packets. During the grinding operation the relative amount of amorphous carbon in anthracite increases from 33.5 to 43%, and the area of the aromatic layers decreases, but the inter-layer spacing d_{002} remains constant (356 pm). Like the earlier workers[14,29–32,40–41], Kirda and coworkers[57] failed to define the material which they termed amorphous carbon.

An analysis of the atomic radial distribution functions[94,95] has led to the conclusion that regions (or domains) of two types are present in vitreous carbon: graphitic, and tetrahedrally bonded (or diamond-like). Similar views were put forward by other workers[45–49,96–102], though others have doubted the presence of diamond-like regions in vitreous carbon. Ergun and coworkers[45–59] concluded from measurements of hardness and density combined with a determination of the width of the diffraction lines that non-graphitising (rigid) carbons contain different crystalline forms of carbon including a substantial amount of micro-structures in which the atoms are tetrahedrally coordinated.

According to the polyadamantane hypothesis[103,104] different carbon atoms in natural coals have different electronic states and different coordinations: ~50% of the atoms are in structural fragments of the complex cycloalkane (polyadamantane) type, ~10% in alkane chains, and only 26–30% in condensed benzene rings.

Another study of atomic radial distribution functions[105,106] has established that practically no condensed aromatic systems are present in vitrinites from bituminous coals containing 77–90% of carbon. It has also been stated[25] that the structure of the vitrinites from anthracite cannot be described by models based on a condensed aromatic macromolecule. It is assumed that all possible types of carbon bond are found in vitrinites from anthracite (as they are in schungite). At least two methods of carbonising coal are known: those tending towards graphitisation, and those tending towards anthracitation (schungitisation) or, more accurately, carbynisation, i.e. the formation of straight or branching chains, ladders, or tapes of three-dimensionally cross-linked macromolecular fragments.

A combination of physical, physicochemical, and petrological studies[9–11] has shown not only that glubular polymeric structures with linear or branching chains are present in the vitrinite part of coal, especially in natural coals in an intermediate state of metamorphism, but also that linear macromolecular fragments are predominant in these structures.

The view that coals are mainly aliphatic has been put forward by several workers[103,107,108]. Aromatic fragments are thought to be present in small numbers, the coal consisting mainly of linear alkane chains. A study[109] of the acetylation of coals of different levels of metamorphism using the chloro-anhydrides of various aliphatic acids (the Friedel–Crafts reaction) has shown that even in the lean coal stage a three-dimensional network has not yet been formed. The volume of graphitoids in natural coal is estimated[110–112] to be less than 10%: the main bulk consists of linear carbon polymers. A mass spectrometric and gas chromatographic analysis of the products of the oxidation of coals by a 40% aqueous solution of nitric acid at 333 K has shown[113] that up to 38% of the carbon exists as linear alkane chains up to 23 C–C bonds in length.

†HTT is the heat treatment temperature.

Thus, in spite of the lack of quantitative agreement on the carbon chain content of natural coals and anthracites, the presence of such chains is accepted by many workers, including adherents to the micellar fringe model. As was pointed out in Ref.111, the make-up of spatially inhomogeneous, structured natural carbons (coals, semi-cokes, anthracites, carbon blacks, vitreous carbon, carbon fibre, schungite, etc.) is complicated by the enormous number of cross-bonds and branching chains, which make it impossible for the material to soften and be converted into a liquid. Being vitreous, this gelled material can only be converted into a highly elastic state by an increase in temperature.

Whittaker and Tooper[114,115], using electron diffraction, found that most of the fragments in vitreous carbon (with HTT up to 3500 K) give diffuse diffraction patterns containing several rings, but a significant proportion gives only spots and rings or even (in 10% of the cases) a sharp pattern consisting only of spots and corresponding to a single-crystal region in the sample. Unexpectedly, the crystalline fragments between 0.1 and several micrometres in size did not have the graphite structure: in most cases their structure was that of carbyne (chaoite, carbon-VI), diamond, lonsdalite, and other previously unknown forms of carbon. On the other hand, patterns corresponding to crystalline graphite were often twinned (with a rotation of approximately 28.5°), suggesting the presence of two crystalline regions in the same fragment (for example, of the lamellar or platelet type).

From these recent and detailed investigations we may draw the following conclusions.

1. The characteristic size of the uniform regions in vitreous carbon is 10–1000 nm, i.e. much greater than the typical crystallite size calculated from the broadening of the X-ray reflexions (L_a, L_c = 1–20 nm).

2. Though a proportion of the carbon atoms is accommodated in aromatic fragments consisting of 1–3 rings[96], a much larger number of C atoms adopts different types of cooperative arrangement (coordination).

3. The presence of different crystalline forms of carbon causes a broadening of the "graphitic" X-ray lines, additional to the "size" effect, since many of the reflexions for these forms lie close to the characteristic graphite reflexions. This interpretation of the broadening of the (002) band and of the enhanced background near this band was suggested in 1965 by Ruland[116], who tried to analyse the intensity of the band not in terms of the distribution of crystallite sizes L_c but in terms of the distribution of intermolecular distances d. This approach was put forward[116] as an alternative to Franklin's artificial postulate of single atomic layers (macromolecules) and of atomically amorphous carbon, assumed to scatter X-radiation incoherently, in a system as close-packed as polymeric carbon. However, this approach was not developed further, and the broadening of the (002) band is now almost invariably ascribed to the crystallite size L_c.

Early work[12–14,28,117,118] on the structure of natural carbons referred also to the γ-band, corresponding to a structure with a periodicity d = 400–500 pm. Abnormally high values of d_{002} are found in many forms of carbon: for example, the values d_{002} = 360–420 pm are typical of carbon blacks[119], and in carbynes the predominant periodicity is 430–480 pm. On the other hand, for polymeric diamond structures consisting of cross-linked atomic layers the typical intermolecular distances d are much smaller. It has been suggested[12,18,117,118] that the γ-band in coals is determined by the intermolecular distance in a packet ~2 nm in diameter consisting of several small aromatic units (the "bitumen" molecules). The high values of d_{002} in other types of carbon have been ascribed to imperfections (curvature) in the aromatic layers, though the existence of these layers was uncritically accepted. The 430 pm periodicity in carbonised polyacenaphthylene (HTT = 460–570 K) was explained in this way[116].

However, an alternative explanation is possible, treating the γ-band as an indicator of the existence of carbon in chains and ribbons[25,26]. This treatment assumes not only the existence of distinct chain fragments, but also whole regions of close and partly ordered packing. For example, the diffraction pattern[120] of amorphous poly(vinyl alcohol) ($-CH_2-CHOH-$, $M \cong 40000$), known to be a chain polymer[36], consists of a single broad peak (with d = 437 pm) for different structural and morphological forms of the polymer (powdered, gelatinous, thin-film, fibrous, vitreous, mesomorphic) at 430–480 K. In spite of the difficulty of formulating a fully convincing interpretation[120], this peak must somehow be a measure of the distance between chains, possibly in a state of free or partially hindered rotation (torsional vibrations). The intensity ratio of the bands with d = 350 and 520 pm has been used[121] to calculate the degree of aromatisation (cross-linking of chains) as a function of time during the thermal oxidation of polyacrylonitrile (PAN) fibres.

The period d = 460–480 pm of the broad band observed[7] in the products of the low-temperature carbonisation of phenolic resins (HTT < 1140 K) has been interpreted[7] as the average distance between narrow tapes of aromatic carbon. This period decreased continuously from 480 to 350 pm as the heat-treatment temperature was increased, i.e. as the degree of aromatisation (cross-linking) of the carbon was increased, and as the narrow tapes and chains grew into two-dimensional atomic layers. This process results in the formation of a three-dimensional network structure. ESR spectral results and measurements of the electrical conductivity for carbonised polyacrylonitrile (HTT = 470–1370 K) were successfully interpreted[122] by a two-phase micro-heterogeneous model which describes the semiconductor as a random mixture of a highly conducting (polyconjugated) phase and an insulating (non-cyclised PAN) phase. The size of these regions in relation to one paramagnetic centre (PMC) was estimated to be ~1.5–20 nm.

A specially wide spectrum of molecular structures and supermolecular formations is observed in the condensation (whether homogeneous or heterogeneous) of carbon from its vapour[123–141], from a plasma[142–151], from a molecular-ion beam[151–156], or from solutions[157–161]. The products (in the form of globules, films, whiskers, etc., depending on the rate of the formation process) may contain any of the known (and some previously unknown) forms of crystalline or amorphous carbon: graphitic (two-layer polytype or normal hexagonal graphite), three-layer cubic or rhombohedral graphite, four-layer diamond, and carbyne. The substructure and some properties of evaporated carbon films are discussed in recent review articles[151,162–164].

VII. CARBYNE AND TRANSITIONAL FORMS OF CARBON

The term carbyne denotes a system consisting only of carbon chains held together by van der Waals forces to form a crystal[165–172]. The chains are assumed to be straight, since the electronic state of each C atom is described by *sp* hybrid wave functions (poly-yne $-C\equiv C-$ or polycumulene $=C=C=$ form). In the total absence of chemical intermolecular bonds (or cross-links) between the chains we obtain the originally postulated carbyne structure: an assembly of linear carbon chains without any chemical bonds between them. To confirm the existence of carbyne in this form we

require material as a single crystal of a size sufficient for extensive structural studies: such single crystals are not available at present. Though a liquid consisting of isolated carbon chains can exist, in principle, it has never been prepared.

Evidently, in real samples the carbon chains are chemically cross-linked by bonds showing various periodicities[173]. Whereas in the description of diamond and graphite systems the concept of intermolecular chemical bonds and associated branching systems (three- or four-function branching) is relatively unimportant, this concept becomes vitally important in the description of carbon chain polymers. Though these systems can be formally classified as transitional forms of carbon[5,6,37], we shall apply the concept of a real carbyne form of carbon (as opposed to the ideal carbyne) to a partially cross-linked three-dimensional polymer having a more or less regular (crystalline) structure and predominantly composed of extensive fragments of linearly polymerised carbon.

This wider definition of the carbyne forms of carbon is more general as well as methodologically more accurate. It includes, in addition to two-function (linear chain) lattice positions, the three- and four-function positions associated with branching (chemical cross-linking). From this point of view the graphitic atomic layers (molecules) and the diamond crystals are the limiting cases of network and chain structures respectively, ideally cross-linked by three- and four-function branching points.

Whittaker[174] interprets the graphitic monolayer in exactly this way: as an assembly of ideally cross-linked (in one plane) carbon chains. It has been suggested[175] that a diamond crystal consists of equal numbers of right and left screw axes, i.e. of helically twisted carbon chains.

In the presence of chemical cross-links between chains of linear carbon polymers the relative position of the chains may not be parallel. This is another important new aspect of the treatment of the carbyne structure. We note that the primary structural fragment is now no longer the two-dimensional layer of sp^2 hybridised carbon, but the chain connecting two nearest lattice points (i.e. the cross-link).

In principle the existence of carbon chains cannot be doubted (see, however, Refs.176 and 177). It has been demonstrated by various methods[178–192], including electron and X-ray diffraction[166–171 193–208].

The fundamental maximum of the energy loss spectrum during electron diffraction (in the 20–50 eV range) by evaporated carbon films prepared by various methods is found[187] to lie near 23 eV, i.e. slightly below the value for amorphous carbon and well below the value for graphite and diamond (27 and 34 eV respectively). The position of this maximum is thought[187] to be a characteristic structure parameter of this type of film. In some samples weak peaks were observed at ΔE = 7 and 33 eV. Annealing and storage of the films causes changes in structure (or, more exactly, changes in the energy loss spectrum).

A peak near 23 eV has been observed[186] for carbyne (in reality, a complex mixture of chain, ring, diamond, and other fragments). However, this result was reported only tentatively, and as possibly due to the presence of traces of oxygen. All the carbons examined (graphite, plasma black, carbyne, diamond) gave a broad band near 17 eV. The carbyne spectrum included two sub-bands, at 16 and 17 eV, reminiscent of the sub-bands found in diamond.

The Raman resonance spectra for poly-yne are interpreted[184] as a clear indication of one-dimensional chains with alternating bonds: the chain length is estimated to be 30 ± 20 C≡C bonds.

The Raman spectrum of natural graphite[180,181] consists of one (Stokes) absorption line at 1570–1580 cm^{-1}. In vitreous carbon, coal, pyrolytic carbon, and carbon black[182] two lines are seen (at 1360 and 1580 cm^{-1}), and in evaporated and white carbon (chaoite, carbyne) three lines[180,181]: at 1360, 1580, and 2140 cm^{-1}. The additional broad line at 2140 cm^{-1} in the carbyne spectrum is ascribed to conjugated acetylene bonds, $(-C\equiv C-)_n$.

Thus all the polymeric carbons show a sharp absorption band at 1570–1580 cm^{-1}, corresponding to a system of conjugated C=C bonds. The i.r. spectra of some samples of paracyanogen $(CN)_x$ also show a single, sharp absorption band at 1570 cm^{-1},[209,210] typical of the C=N bond[211], and therefore this band cannot be used to establish the electronic structure of our systems. It has been suggested[210,211], from X-ray diffraction results, that paracyanogen also has a layer lattice of the graphite type, with alternate C atoms replaced by N atoms, and the black colour and high stability of paracyanogen have been ascribed to resonance interactions involving electron transfer. The C–N interatomic distance in paracyanogen (136 pm) and the C–C distance in graphite (142 pm) are not very different: the difference between the interplanar spacings (~450 and 335 pm) is much greater[210,211]. On the other hand the colour of crystalline carbyne particles is white.

Obviously, all possible electronic states in condensed carbon atoms cannot be reduced to three types, with sp, sp^2, and sp^3 hybridisation. For example, s^2p^2 hybridisation is also possible (bivalent carbon model[7,212]), as well as multi-step hybridisation of already hybridised states, etc. Theoretical calculations suggest that the following structures are relatively stable: four-coordinated planar carbon (singlet biradical)[213], diamond-like three-coordinated amorphous carbon[135], pentagonal pyramids (a half-sandwich, positively charged in the cyclopentadienyl ring base of the pyramid[214]), and other electronic states[215,216].

Even the electronic structure of graphite is still being discussed[49,63–65,217], and doubts have been expressed on the dynamic equivalence of the σ-bonds in the layer, on their planarity, and their hexagonal symmetry. An orthorhombic elementary cell has been suggested[49,63,64], with a = 240.9, b = 433.9, c = 670.8 pm: the so-called quinoid structure, in which two-thirds of the C–C bonds are 145.3 pm long and the remaining one-third 135.7 pm, the bond angle being 112, 124, and 124°.

It has also been shown that the specific heat $C = f(T)$ curves of different polymeric carbons lie in the following (increasing) sequence: diamond, graphite, anthracite (and schungite), carbyne, and heat treated polyfurfural (HTT = 790 K, a mainly linear polymer)[178,179]: the heat of combustion of carbyne, Q = 84.54–88.80 kcal $mole^{-1}$, is significantly lower than those of graphite (94.05 kcal $mole^{-1}$) and of diamond[173]. The conclusion is that carbon in chains is thermodynamically more stable than graphite or diamond[173].

The specific heat of these materials at very low temperatures (0.44–4.5 K) has been found[218], surprisingly, to obey the law $C = \alpha T^3 + \gamma T$. The linear term almost certainly denotes the presence of a one-dimensional phonon spectrum. After neutron irradiation the coefficient γ increases, and α decreases (in parallel with degradation of the vitreous carbon)[219].

X-Ray and electron diffraction studies[220–226] of natural or artificial graphites had shown (even in the 1930's and 1940's) anomalous reflexions which could not be assigned to known crystalline modifications of carbon. In order to account for these reflexions various graphitic superstructures had to be postulated, though they could not be independently confirmed.

The observation[102] in the electron diffraction patterns from similar vacuum-evaporated films (of density 2.4 g cm^{-3}) of eleven diffuse haloes could only be explained by assuming that the intensity maxima were neither from graphite nor from diamond structures.

An electron diffraction camera (ER-100) has been used[227–230] also to study carbon films evaporated by an electron beam under the following conditions: vacuum ~5 × 10^{-7} mmHg, substrate NaCl or $BaCl_2$, T = 310–340 K, angle of incidence of the electron beam on the substrate 60°, rate of condensation 0.2–0.3 nm s^{-1}, film thickness δ = 10 or 80 nm. The electron diffraction patterns showed six haloes, the strongest being for d = 455 pm with δ = 10 nm and d = 485 pm with δ = 80 nm. The authors conventionally assumed that these large "interlayer spacings" are due to the insertion of carbon atoms between the graphite nets, giving distorted and highly supersaturated interstitial solid solutions of carbon in carbon. The regions of coherent electron scattering for which L_a = 1.2 nm and L_c = 0.8 nm were identified with strongly distorted graphite crystals in which the regularity of the mutual orientation of neighbouring graphite nets had been lost.

The atoms in evaporated films are often assumed to be grouped in diamond-like and graphite-like fragments[102,133,163,231]. In recent years it has become clear that thin carbon films (usually graphite-like[162–164,232,233]) can be in a polycrystalline cubic (diamond) phase completely free from graphite impurities when prepared under special conditions[143–159,234], the individual diamond crystallites reaching 5 μm dimensions[152–156]. However, the possible carbon structures in evaporated films are not limited to graphite and cubic diamond[187,235]. Fragments of lonsdalite and other unidentified ("intermediate") phases have been detected[149,236] in substantial amounts in carbon deposits, together with the cubic diamond phase. These phases were believed to be chaoite (α-carbyne). Cubic graphite also has been observed in condensed deposits[237,238]. But in most cases the investigators were "forced to discover" new crystalline forms of carbon[170,171,194–208,237–246].

Thus Aust and Drickamer[237] reported preliminary data on the synthesis of a new crystalline (high-pressure) carbon phase, formed by compressing a single crystal of graphite to 150 kbar. They described the crystal as cubic (a = 554.5 pm), with n = 24 atoms in the elementary cell and a density ρ = 2.80 g cm^{-3}. Later work, however, showed that these results were erroneous.

There are reports[241,242] that the condensation of a carbon plasma in a vacuum on a freshly cleaved KCl single crystal gives, in addition to a finely divided diamond-like deposit of particle size 1–2 nm (giving diffuse electron diffraction rings corresponding to d = 209, 115, 74, and 59 pm), also a scattering of faceted microcrystallites between 10 and 300 μm in size, giving electron diffraction patterns of the monocrystalline and the polycrystalline type. These crystals were indexed in the body-centred cubic lattice: a = 427.9 pm, n = 16, ρ = 4.1 g cm^{-3}. This new crystalline carbon phase, with a density 15% higher than that of diamond, is thought[241,242] to consist of close-packed slightly distorted tetrahedra.

The carbyne family continues to grow. At least six varieties of carbyne (polytypes) are known at present[169–171,194–201,207,208]: according to Whittaker[174] there may be eight.

A recent paper describes the synthesis of chaoite[247] ("a new hexagonal allotropic form of carbon") from vitreous carbon wafers compressed by a shock wave to 100 GPa. The structure was identified by electron diffraction (a = 893.7 ± 4.0 pm). The possibility of homogeneous nucleation and selective growth of diamond and other forms of carbon had been suggested[129–133], including carbyne phases, if conditions in the gas phase are optimised for a particular form: for example, laser irradiation of liquid hydrocarbons was found to favour the formation of microscopic diamond and carbyne granules.

Crystalline carbon in the carbyne form has been detected in thin lamellar streaks and in graphitic deposits[248]. As Whittaker points out[248], carbynes are not a rare form of carbon: their natural distribution is relatively wide.

We should stress that carbynes are not necessarily always crystalline. Their degree of order (or crystallinity) can be arbitrary.

The "rediscovery" of carbon has continued, at an increasing rate, during the past few years. We can expect, as a result, new and truly "polymeric" concepts to be developed in the structural physics of carbon. Thus, it has been established[245] in principle that carbon can exist in new crystalline structures showing sp^2 hybridisation of the atomic orbitals and topologically different from known modifications (diamond, graphite, and carbyne). These structures can arise through the formation of covalent bonds (regular cross-links) between helical carbon chains. Though the formation of these carbon polymers is kinetically hindered, the chains are thermodynamically stable owing to the presence of high energy barriers which prevent the conversion of the system into graphite or diamond.

Further new and surprising properties of carbon in thin films has been observed. For example, the colour of vacuum-evaporated films previously heat treated at 550 K slowly changes (at ~1 mm min^{-1}) from black to grey after a localised pin-prick has been applied[249]. The thicker the film, the faster is the motion of the colour-change front (within the range δ = 15–200 nm). Simultaneously with the colour change, the electrical conductivity increases by an order or more. Heat treatment has a similar effect. After this structural change the carbon films become amorphous, or are converted into a mixture of interpenetrating fine particles of graphite and diamond phases.

The instability of the electron distribution (for example, in a fixed configuration of the nuclei) occasionally manifests itself as the reversible memory switching effect shown by many disordered oxide and glass systems[250] in evaporated carbon deposits[251], in vitreous carbon[252], etc. The electrical resistance of these systems suddenly falls, following the application of a voltage above some threshold value (2–10 V), by several orders of magnitude (for example, from 450 to 1.8 kOhm). Both states (high-resistance and low-resistance) are metastable, and can be "remembered" for several days[250–253]. This means that the electronic subsystem of the material can be in one of several metastable states (energy levels), i.e. the material shows non-equivalence of the C atoms (in particular, a variable degree of ionicity), alternation of the interatomic bonds, and changes in the type of localisation and distribution of the electrons surrounding the atomic cores. It is suggested[252] that in the presence of an electric field thin needle-like conducting channels are formed in the film, as in the development of low-temperature trans-polarisation in ferroelectric materials[254]. (The same explanation has been applied to the switching effect in filamentary Sb_2S_3 single crystals[255].) However, the nature of the low-resistance state is still under discussion[250,256].

The ESR absorption of different forms of carbon is due to the presence of at least two types of PMC, differing in geometric configuration and in internal structure. The narrow ESR signal is assigned[257] to unpaired, delocalised electrons, located in the aromatic regions of cyclically polymerised carbon, whereas the origin of the broad signal is thought to be a set of PMC localised in the "amorphous" phase of the system: small oxygen-containing or (more probably) carbon radicals with planar or linear π-conjugation. Samples of vitrinite from Donets gas carbon[258] previously heat treated

for 30 min at 900 K (i.e. having a maximum concentration of PMC) give a vacuum ESR signal (at 10^{-4} mmHg) whose intensity varies steeply and reversibly with the measurement temperature: it falls about 10-fold when the sample is cooled to 290 K, and returns to its initial value when the sample is re-heated *in vacuo* within the resonator of the spectrometer. As the intensity of the broad signal increases, a narrow ESR signal appears, and grows. On the other hand, if the heating and cooling cycles in the cavity are carried out under ordinary conditions (rather than in a vacuum) the intensity of the ESR signal becomes a maximum at 470–570 K. The increased intensity of the ESR absorption of heat treated vitrinite samples on cooling has been explained[258] not by the formation of free radicals or by irreversible rearrangements of the molecular structure, but by changes in the collective state of the electronic subsystem (possibly, of π-associations) under the influence of temperature.

More recent work[122,257–261] has tended to rely on improved methods of analysing the ESR spectra, using the entire spectrum rather than the shape of a single line, and allowing for complex, polymodal spectra, in order to extract information on the size of the structure fragments (radicals) of various types. The concept of clustering of paramagnetic centres has been firmly established in a recent paper[261].

Whittaker and Kintner[197] showed that the high-temperature emission (sublimation) of carbon at $T = 2800–4000$ K occurs mainly as graphite and carbyne particles, giving a visible Tyndall effect. In all types of carbon examined (graphite, coke, and carbon black compositions with spectroscopic carbon, pyrolytic carbon, or vitreous carbon as a binder) the weight of sample lost through the emission of particles was 60–90% of the total weight loss. Particle size varied from molecular (1–100 nm) to 60 μm.

Cypres and coworkers[262] have reported a thermogravimetric study of the hydrogenation kinetics ($C \rightarrow CH_4$) of high-purity (nuclear) graphite, i.e. of the gasification of graphite at atmospheric pressure in a stream of pure hydrogen at 1220 K in the presence of finely divided metallic iron as a catalyst. The rate of gasification was directly proportional to the concentration of iron in the sample. Graphite and α-iron were detected in partially gasified samples by X-ray diffraction. The diffraction patterns included three anomalous lines which could not be assigned to any known carbide. By using electron diffraction the following structural periods d_{hkl} (in pm) were observed for the new phases in different orientations:

214.0; 123.9; 106.3; 75.4; 70.0; 348.7; 238.9; 118.0; 79.4; 461.5; 261.5; 174.3; 152.8; 132.6; 98.1; 88.0.

The periods corresponding to the strongest reflexions are underlined. No attempt was made to discuss the nature of these new phases, though the correlation between some of the periods and those given by Whittaker and Wolten[198] for carbon-VI (carbyne) is striking ($a = 924$ pm, $c = 1224$ pm). Carbyne forms of carbon, more stable towards hydrogen, may be formed from graphite in the H–C–Fe system.

Carbynes are only beginning to gain general acceptance. They have tended to be ignored in the technical as well as in the scientific literature because of the reluctance to accept the exaggerated concept of an artificially graphitised polymeric carbon[16–20,23–25,28–34] (highly dispersed, turbostratic, defective, fine-, crypto-, or paracrystalline, etc.).

In spite of these difficulties approximately 100 papers on the structure, synthesis, properties, and even possible applications of carbyne have already been published, including several reviews[166–168,172,263,264]. Nevertheless carbyne remains a chemical curiosity: so far no atomic structure calculations have been carried out for any of its many modifications, nor have electron distribution calculations been attempted. The history of the discovery and of the gradual acceptance of carbyne (from the scientific and the practical point of view) is itself a fascinating study. By now the preparation of carbyne and the problems arising from its structure and properties have been integrated into the general problem of elemental (polymeric) carbon.

VIII. CONDENSATION OF CARBON AND LAMELLAR FORMATIONS

In general, graphite, carbon black, diamond, and carbyne can be formed from the gas phase (including plasmas and ionic–molecular beams). Evidently, the type of carbon formed is determined by kinetic rather than by thermodynamic factors: the intensity of the flow of carbon atoms being deposited, their energy, the degree of clustering (cooperation) in the flow, the structure and temperature of the substrate, the pressure and composition of the gaseous medium, etc.

In a d.c. arc carbon whiskers up to 3 cm long and ~10 μm in diameter can be formed[53]. According to recent evidence a whisker is a scroll of coaxial, helical carbon layers oriented normally to the substrate, i.e. parallel to the growth direction (axis) of the whisker. Surprisingly, a thin "leader", ~20 nm in diameter, grows first, and is subsequently thickened[265].

Characteristic spirals have been observed in synthetic and in natural graphites[266]. It was suggested[267] that graphite crystals grow by the addition of atoms or atomic groups to the edges of crystal faces. Though several crystallisation centres are thereby buried, some growth steps ~10 nm high are also formed. These spirals are easily seen in an electron microscope: they point to the pyramidal growth of layers in artificial graphite single crystals[268,269]. Conical graphite crystals consisting of thin packets of graphite layers successively wrapped round the *c* axis have also been observed. Their formation is interpreted as evidence of a spiral growth mechanism of the crystal.

Growth from acetylene-containing gases[124,141] on molybdenum disks heated by radiation from an LG-25 laser has yielded hollow carbon whiskers having a "bamboo" morphology, i.e. with a longitudinal periodicity. Straight, bent, or helically shaped whiskers have been obtained. According to diffraction measurements the graphite basal planes are stretched along the growth direction of the whiskers, which explains their high tensile strength. Electron diffraction measurements showed that the whiskerisation of carbon filaments 6 μm in diameter produces, in addition to graphite, also carbyne and other unidentified carbon phases having periods $d = 455$, 390, 340, 283, 262, 247, 213, 158, 147, and 123 pm.

The formation of hollow carbon whiskers with cylindrical internal cavities 2–50 nm in diameter has been reported also from other laboratories[270]. The filament body consists of two coaxial parts. One, adjacent to the axial cavity, is composed of long carbon layers extending along the axis, which apparently grew during the early stages of the process. The second (external) part of the filament is probably formed by pyrolytic deposition of "amorphous" carbon during a subsequent stage.

The graphitoid model of the growth mechanism and of the inner structure of carbon whiskers is probably far from correct. Thus, filamentary diamond crystals can also be grown from a vapour–gas mixture containing carbon[124,271,272]. In general the initial stages of the heterogeneous condensation (polymerisation) of carbon and the inner structure and morphology of the resulting product (carbon black, diamond,

graphite, carbyne, and "hybrid" forms) have not yet been studied systematically.

In this respect it is interesting to note[273] that the "hexagonal planar nets" in carbon deposits obtained by the decomposition of *p*-xylene in a glow discharge are rotated by 90° and oriented with their plane at right angles to the deposition surface. Growth from the gas phase of graphite scales with their basal plane normal to the deposition surface has also been reported[140].

High-resolution electron microscopy has been used to study partially graphitised film[70]. The films were found to contain vertically oriented one-, two-, and three-layer "graphite platelets", with their *c* axis perpendicular to the primary electron beam. The micrographs of the two- and three-layer graphite platelets showed that the inter-layer spacing in these very thin crystallites is significantly greater than in larger crystals. Convincing evidence was obtained that this observation is not a photographic artefact, but is genuinely due to a weakening of the van der Waals forces between layers in very thin crystals.

Similar features have been observed[274] in the growth of diamond-like films from the gas phase. The films were either fully microcrystalline, with randomly oriented grains, or well textured, with the (110) texture axis perpendicular to the substrate (consisting of the (111) face of a natural diamond crystal). However, deposition from ionic beams on polycrystalline substrates gave mainly diamond crystals with a (111) orientation[152-153].

Samples prepared by static compression of powdered graphite were recently found[275] to contain ~70% of lonsdalite, up to 20% of diamond, and up to 10% of graphite. One-dimensional disorder effects in the disposition of the (001) basal planes of lonsdalite have been detected. The powders were found (by transmission electron microscopy) to consist of flat particles, reflecting the platelet structure of the initial graphite. The textures observed on the electron diffraction patterns indicated (111) diamond planes and (001) lonsdalite planes perpendicular to the surface of the particle (which before the phase transition consisted of a (001) graphite plane). The observed orientations could have been caused by a martensitic transformation of the graphite by the mechanism known as longitudinal layer bending. During the graphite → lonsdalite transition equivalent systems of (100) graphite planes are transformed into (001) lonsdalite planes, and the [001] direction in graphite becomes the [100] direction in lonsdalite.

The block size of the lonsdalite, revealed by dark-field electron microscopy in the (103) reflexion, was about 4 nm, and that of the diamond in the (111) reflexion was 10–15 nm. The lattice parameters were: $a_l = 251.6 \pm 0.5$ pm, $c_l = 418 \pm 2$ pm, $a_d = 355.8 \pm 0.5$ pm. The latter value is substantially lower than the corresponding value for perfect, large diamond crystals ($a = 356.70 \pm 0.01$ pm).

Lastly, there are many reports[168-170,198,207,208,248] of individual crystalline carbyne particles with well developed facets and a platelet shape (lamellar or scale-like). It is thought that the partially cross-linked carbon chains are oriented at right angles (or at an angle which can vary by discrete amounts) to the basal face of the lamella. It follows that, as in the crystallisation of organic macromolecular chains (for example, polyethylene), the fundamental and simplest morphological unit in polymeric carbon is a thin, transparent particle (lamella) ~10 nm thick. The size of the lamella in the two other dimensions (i.e. in the direction of the basal plane) can be much greater: up to several tens or even hundreds of micrometres. The surface of these faces is fairly even, flat, and smooth, without any visible steps. The lamella as a whole can be sharply bent, folded, and twisted (Fig.3). Several lamellae stacked together produce piles, pyramids, and aggregates of the fan and bundle type (Fig.4). In general carbyne particles are conglomerates of separate lamellae, showing varying degrees of complexity.



Figure 3. Lamellar particle of α-carbyne (×20000).

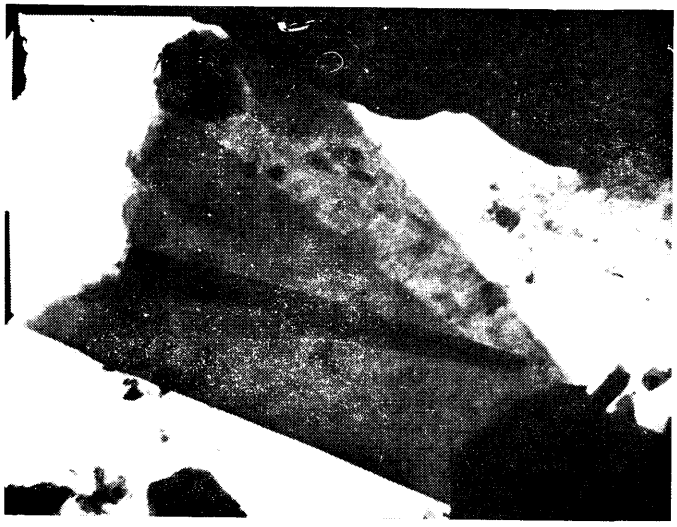


Figure 4. Aggregate of lamellar carbyne particles (×10000).

If carbon vapour is condensed on a cold substrate sufficiently slowly the product consists mainly of carbyne forms of carbon. The deposit is an assembly of fragment, mostly platelet-like. The thicker particles (stacks of lamellae,

Fig. 5) break up into several thinner particles, like schungite, when fractured by compression[276]. This observation convincingly demonstrates that large carbyne particles have a layered inner structure.



Figure 5. Layer structure of a condensed carbon particle (×2000).



Figure 6. Typical electron diffraction pattern of a carbyne lamella (with Au reference rings).

It has also been observed that under the influence of the electron beam an initially sharp diffraction pattern (spots and rings, Fig.6) often becomes gradually more diffuse, and after some time (~1 min) disappears. Amorphisation by electrons has been observed also in organic chain polymers[35], but not in diamond or graphite crystals. After irradiation the basal surface of the lamella develops pits ("sores") of various shapes. Similar fibrillar "vacuoles" have been observed by other workers[198,274]: the former were produced by radiation, but the latter were present in the sample as deposited from the gas phase, and they had almost invariably a regular conical shape.

Filamentary particles are occasionally detected in the scanning electron microscope[207]. This has led to the suggestion that individual carbon chains (molecules) become associated into a bundle of uniform composition[173,263]: a kind of primitive fibril. In this case dense particles are formed by the combination of submicroscopic filamentary particles[207]. Obviously these are the fragments which can be observed experimentally (to a varying extent) in all forms of condensed carbon, and they are the main structural units at the second (supermolecular) organisation level.

By combining dark-field contrast techniques with scanning electron microscopy in the transmission mode (which can sample a region only 0.24 nm in diameter) Isaacson and coworkers[277] have studied the structure of carbon films 0.68 nm thick condensed from the vapour phase, i.e. consisting of only 2–4 atomic layers. Both stepped and smooth regions over 3 nm in diameter were observed.





Figure 7. Lamellar microstructure of heat treated anthracite (HTT 3200 K): *a*) electron micrograph (×25000), *b*) electron diffraction pattern.

Carbon particles obtained by reducing polytetrafluoroethylene with sodium amalgam[278] consist of lamellae reminiscent of those found in polytetrafluoroethylene spherulites, a few tens of nanometres thick.

In anthracites the layer structure can be observed at all levels[111,112], from the optical (platelet shaped deposits) to the molecular. An electron micrograph and the corresponding selected-area diffraction pattern of thermo-graphite particles[279] prepared at 3100 K are shown in Fig.7. Platelets 10–30 nm thick are clearly visible. The individual lamellae consist of a parallel stack of aromatic layers parallel to the large faces. On the other hand the chains in the carbyne lamellae are oriented (apparently) at right angles to these faces, since most of the selected-area electron diffraction patterns have hexagonal symmetry.

A very unusual structure has been observed[280,281] in pitch cokes: ultrasonic dispersion can split off platelets (lamellae) thin enough to be transparent to the electron beam. The boundaries of the lamellae are clearly visible because the optical density is uniform within a single stack but it changes in discrete steps over the micrograph as a whole. Selected-area electron diffraction patterns from lamellar particles of unheated petroleum coke have shown[282] (002) and (004) reflexions from planes oriented almost normal to the planes responsible for the (110) and (100) reflexions, as in the case of mesophase particles. Hence the electron beam was aligned almost parallel to the atomic layers. These results were interpreted by assuming an oblique exposure, with the particles oriented preferentially at right angles to the substrate.

It has been shown[283] that irradiation of a thin carbon film with an Ar ion beam of 1.2 MeV energy produces surface corrugations, revealed by the appearance in the electron diffraction pattern of "three-dimensional" reflexions of the (112) and (002) type in addition to the basal ($hk0$) reflexions. It was also noted[284] that graphite single crystals are degraded in discrete steps rather than continuously when irradiated with neutrons: polygonisation into smaller crystals is the most likely mechanism.

Local electron diffraction patterns from lamellar particles in a single crystal of carbyne (Fig.8) can show a large number of weak but quite sharp rings corresponding to basal reflexions from graphite (probably deposited epitaxially on the large faces of the carbyne lamellae). In this case the system is evidently two-phased: carbyne, and a thin but extensive layer of relatively well ordered graphite. We should note that even Franklin[31] often observed one or two sharp lines corresponding to the periods d = 342.6 and 336 pm against the background of a diffuse (002) line in non-graphitising forms of carbon (from poly(vinylidene chloride) or sugar charcoal, 83.1% C, HTT = 2300–3300 K). A sharp peak against a diffuse (002) background is clearly visible also in heat treated wood charcoal[285], and in neutron-irradiated graphite[286,287]. Two-phase graphitisation is examined in depth in Refs.288 and 289.

This phenomenon clearly suggests the presence of relatively extensive crystalline regions ("islands") within the main, more amorphous material, and has been interpreted as heterogeneous graphitisation of the carbon vy evaporation and condensation on crystallisation centres, by transport of the carbon in the form of volatile compounds with hetero-atoms, and by other mechanisms[27,31,37,290–292]. However, an alternative agency leading to "heterogeneous graphitisation" is the presence of internal surfaces, and in particular the large faces of lamellar formations. By analogy with organic polymers we may assume that the lamellar structure in carbon is relatively labile, and easily destroyed. In a styrene–isoprene copolymer the largest period (60 nm) begins to increase quite rapidly[293] at temperatures as low as ~470 K, reaching 120 nm at 520 K: at the same time the number of low-angle reflexions decreases from 10 to 3. Above 520 K the low-angle diffraction pattern disappears completely. This behaviour suggests that the lamellar structure is not re-established when the molten polymer is cooled.

Brief (10–20 s) heating of oriented polyethylene samples 4.5 K above the melting point was also found[294] to cause a substantial increase in the large period: from 32 to 90 nm.

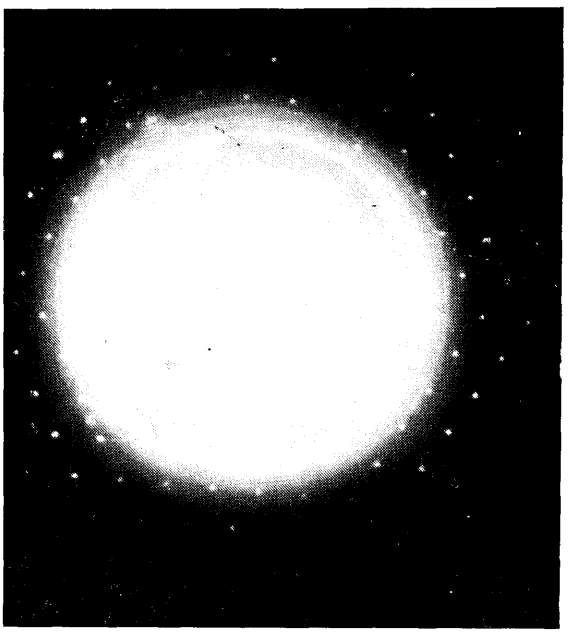


Figure 8. Selected-area electron diffraction pattern of a lamellar particle of deposited α-carbyne.

Experiments on the "pure" condensation (polymerisation) of elemental carbon under fully controlled conditions so far reported are few. Nevertheless the following conclusions are legitimate.

1. White carbyne deposits are obtained, apparently, under the milder condensation conditions: fairly high vacuum, low flux and energy of the atoms or groups of atoms (or ions) impinging on the substrate, low rate of deposition. The chains appear to grow normally to the surface without developing cross-links. Univalent hetero-atoms (e.g. hydrogen) in the surrounding medium may stabilise the chain and prevent cross-linking. These conditions occur during laser irradiation (in a vacuum) of pyrolytic graphite platelets, followed by condensation of the vapour on another platelet[204,207] or near the rim of the resulting crater[180–183,199,200]. They also occur during the normal evaporation (emission) of carbon from the hotter parts of the surface and condensation on the cooler parts[198], during the evaporation of spectroscopically pure carbon in an electric arc in a vacuum evaporator, followed by free crystallisation of the vapour on a freshly cleaved rocksalt crystal[208], during the synthesis of carbyne from organic compounds in a glow discharge[244], in a low-temperature plasma[142,241,242], etc.

2. Diamond (lonsdalite), on the other hand, is obtained under less mild condensation conditions: high energy of the impinging atoms or ions (which thus penetrate deep into the already deposited film and perturb its structure, "mingling"

the carbon atoms and favouring chemical cross-linking). The substrate in this case plays only a minor role. This probably explains the fact that diamond rather than carbyne films are almost invariable obtained from molecular (or ion) beams in a vacuum[143-156]. It is also found[295] that the bombardment of thin graphite films partially ordered (in three dimensions) with Ar^+, N^+, He^+, and Ne^+ ions of average energy 50–80 keV converts the sample into a new modification of carbon which has a low electrical conductivity, a high hardness, and a face-centred cubic lattice of period $a = 369$ pm (as compared with $a = 356.70$ pm for diamond). A chemically active surrounding atmosphere and a high pressure also favour the cross-linking of carbon atoms and chains into diamond forms of carbon[236]: this is probably the mechanism of the synthesis of diamond from the gas phase by Deryagin and Fedoseev's method[124-133,136-139]. Pressures (under shock tube conditions) up to 120 GPa have also been shown to convert graphite into diamond, and diamond into a metallic carbon phase[296,297]. Vitreous carbon under shock compression is converted into an ordered state (probably a diamond phase[296]).

3. Under ordinary (moderate) conditions, with a fairly high concentration of gas-phase atoms of not too high energy, layer polymers of carbon are formed: pyrolytic graphite, carbon black, and pyrolytic carbon, with a high or a low concentration of inter-chain and inter-layer chemical bonds (cross-links) in a regular arrangement.

IX. CONCLUSIONS

Solid carbonaceous materials had traditionally been classified into three categories: diamond (lonsdalite), crystalline graphite, and amorphous carbons.

According to well established classical views substances such as blacks, coals, cokes, schungite, pyrolytic carbon, evaporated layers, etc. are systems consisting of small graphite fragments (crystallites) embedded in random orientations in the amorphous material. The basic component of all forms of carbon (except diamond and lonsdalite) was thought to be the aromatic two-dimensional layer (or macromolecule). The difference between different substances was purely quantitative, depending on the difference in size and shape of these layers, as well as on their degree of perfection (flatness) and the order of their mutual orientation. Obviously, diamond and lonsdalite are an exception to the general rule. The diamond type of lattice forms a special subgroup among the symmetry space groups defined in crystallography and in crystal chemistry.

The temptation to fit all the multitude of non-diamond polymeric forms of carbon into the Procrustean bed of graphite is still strong. The discovery of long tape-like aromatic fragments and diamond-like inclusions, the amorphous fringe concept (i.e. carbon chains and extensive layers (macromolecules) connecting different graphite crystallites), the concept of coexisting atoms of different types (with sp, sp^2, or sp^3 hybridisation of the atomic orbitals) in the so-called transitional forms of carbon, even the discovery of new crystalline (carbyne) forms of carbon have rocked the foundations of the graphitoid conception of the artificial graphitisation of polymeric carbon but have failed to destroy it. The sharpest criticism of this conception arose from studies of the nature of coals, in which linear carbon polymers were suggested as an alternative to the graphitons (or aromatic layers).

In this review we have tried to demonstrate the limitations of the graphitoid ideas as applied not only to coals but to all forms of carbon by analysing experimental data and theoretical models. Crystalline graphites and diamonds (in two, three, or many layers) are only a few of the forms in which polymeric carbon can exist: they may be the commonest, but not necessarily the most stable. This conclusion is no longer in doubt. Crystalline carbyne, which contains carbon chains between branching points, has as much physical reality as graphites and diamonds. Whereas in the traditional approach the very suggestion of transitional forms of carbon in a crystalline state (regular type) appears absurd, experiment shows the opposite, namely that an immeasurably large number of crystalline forms of carbon can exist. This phenomenon is yet another illustration of the many unique aspects of carbon as an element: it is not surprising that life on earth should have developed through the biochemistry of its compounds.

The electronic subsystem of a cooperative system of carbon atoms is very labile. It is characterised by a large number of metastable states: transitions between these states are possible, giving switching effects, even for a given (fixed) configuration of the atomic nuclei. Equally numerous are the possible types of electronic state of the atomic "loggias". The coordination (cooperation) between atoms can differ, the coordination number z usually varying between 2 and 4, though other values are possible. In this sense a one-component substance consisting of single carbon atoms should more correctly be treated as consisting of atoms of different types, since the atoms are not identical. The possible combinations of even three kinds of carbon atom (in reality, far more than three) are very numerous and varied. They amount to a set of systems of indeterminate composition and both regular and non-regular structure.

Some crystalline forms of carbon may have very unusual electrophysical, magnetic, or mechanical properties: they can be superconductors, conductors, semiconductors, or insulators. The strategic objectives of current carbon research include the development of a systematic approach to a unified scientific description of cooperative phenomena in elemental carbon, the controlled synthesis of carbon crystals having prescribed properties, and the study of the structure and properties of these crystals.

Diamond has long been used as a super-hard material, and graphite also has found widespread practical applications. Carbyne is now beginning to establish itself. Polymeric carbon, in its enormous variety of forms and modifications, will undoubtedly become a leading technological material. The strong tendency of carbon towards localised cooperation (polymerisation), increasing with temperature, gives it an advantage over all other polymers, which are degraded by heat.

The general progress in carbon science and the developments in the carbon industry have created new prospects for the application of different types of carbon in electronics, the aircraft industry, space technology, medicine, constructional materials, etc.

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Highly Anisotropic Molecular Solids

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The physicochemical properties of quasi-one-dimensional crystals formed by charge-transfer complexes, radical-ion salts, and coordination and organometallic compounds are examined. The characteristics of the electrophysical, optical, and mechanical properties of these compounds due to the crystal structure and the nature of the movement of the electrons and (or) holes in them are discussed.
The bibliography includes 230 references

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I. INTRODUCTION

The development of the physics and chemistry of the solid state involves at the present stage the study of new classes of substances. The greatest advances are associated with the investigation of low-dimensional molecular solids—quasi-one-dimensional and quasi-two-dimensional. By quasi-one-dimensional systems, one understands systems exhibiting a high anisotropy of their physical properties: electrical resistance, magnetic susceptibility, reflection coefficient, Young's modulus, and others. The electrons in such systems can move mainly along one direction (filament) crossing from one filament to another only in rare instances either as a result of jumps or by tunnelling. Such systems are attractive because one can neglect to a first approximation the interaction between the filaments and one can consider one-dimensional movement for which there exist a whole series of many-particle models susceptible to exact solution.

The problem of quasi-one-dimensional systems arose after the publication of the interesting although erroneous study by Little[1]. This was associated with the problem of high-temperature superconductivity, namely the possibility of the operation of the exciton—electron mechanism of superconductivity. Little put forward a specific version of this mechanism (known as the Little model) comprising a polymeric highly conducting organic linear molecule containing side chains—monomers with a high polarisability. On the basis of the one dimensional model, Little applied the Bardeen—Cooper—Schrieffer (BCS) theory, which constitutes a satisfactory approximation in the three-dimensional case, to the calculation of the critical temperature of a superconducting junction and obtained the fantastic value $T_{cr} = 2200$ K. In other words, a system satisfying Little's model must be a superconductor over the entire temperature range of its existence.

The results of this study were subjected to a thorough and just criticism (see, for example, Refs.2–4), but it created such an enormous impression that a search was immediately begun for systems formally satisfying Little's model. The initial aim was to increase the critical temperature for superconduction: this led to the creation of new branches of the physics and chemistry of the solid state—the physics and chemistry of quasi-one-dimensional systems. Substances with a high anisotropy in physical properties were discovered primarily among the class of molecular complexes—charge-transfer complexes (CTC) and radical-ion salts (RIS). As early as 1962, the radical-anion salts of 7,7',8,8'-tetracyanoquinodimethane (TCNQ) with simple and complex compositions [Kt^+TCNQ^-, $Kt^+(TCNQ)_2^-$, and $Kt_2(TCNQ)_3^{2-}$, where Kt is the metal or organic base action], were described in a review[5]. A characteristic feature of systems of this kind is an unusual quasi-one-dimensional nature of the packing of the salt components in the crystal in which the TCNQ molecules form infinite columns of interleaved and non-interleaved types (Fig.1).[6,7]

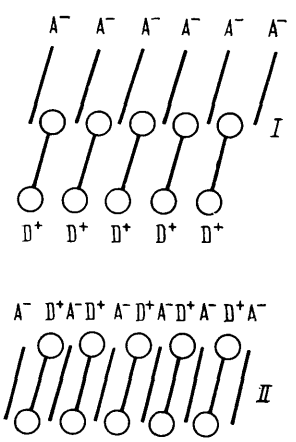


Figure 1. Types of molecular packing of CTC: II) interleaved type; I) non-interleaved type; A = acceptor; D = donor.

In 1968 Krogmann obtained planar mixed valence complexes with metal—metal bonds based on platinum cyanide (Krogmann salts)[8,9]. These salts have the composition $K_2Pt(CN)_4.X_{0.3}\cdot nH_2O$ (X = Cl or Br) and exhibit a distinct anisotropy of their

electrical, magnetic, and optical properties[10-12]. Compounds with a similar structure were obtained by Krogmann on the basis of complex platinum oxalates, for example, $Mg_{0.82}\cdot[Pt(C_2O_4)_2].5.3H_2O$ and $K_{1.6}[Pt(C_2O_4)_2].2H_2O$.[13,14] Highly conducting compounds with a quasi-one-dimensional structure, based on iridium carbonyl halides having the composition $K_n[Ir(CO)_4Cl_m]$, have been described[15]. The physical properties of the above compounds have been examined in detail in a review[16] and therefore not discussed here. Particular attention has been devoted to the properties of organic conductors, their synthesis, and purification in the review of Khidekel' and Zhilyaeva[17].

The present review surveys the results of experimental and theoretical studies on highly anisotropic molecular solids (excluding polymers) obtained after the publication of previous reviews[16,17].

II. THEORY OF LINEAR CONDUCTING SYSTEMS

Numerous studies have been made on the nature and stability of the metallic state in quasi-one-dimensional systems. It was therefore necessary to develop new methods of calculation taking into account the interaction between one-dimensional filaments, which is very significant for phase transitions in quasi-one-dimensional crystals (phase transitions are impossible in a rigorously one-dimensional crystal[4]).

In order to explain the electrical properties of charge-transfer complexes (CTC), many different models have been proposed. The most natural model is that of bilinear organic conductors in which the conductivity of the crystal is assumed to be additive to a first approximation. On the basis of this model, Phillips[18,19] explained the characteristics of the electrical properties of organic conductors by the appearance of domains with a Peierls structure. It is assumed that the sizes of the Peierls energy gaps are different for donor and acceptor columns and the lattice periods are therefore also different. The domains with a Peierls structure are formed when the difference between $E_A(T)$ and $E_D(T)$ is small. This type of structure disappears in a first order-phase transition. The Phillips model is applicable to TCNQ complexes; in particular, it explains the observed temperature dependence of the electrical conductivity $\sigma(T)$, which varies in proportion to T^{-n} $(n>1)$ when $T>T_D$. The domains alternate with metallic regions whose length is of the order of hundreds of angstroms. The charge can migrate not only along the chains but also between them—via jumps.

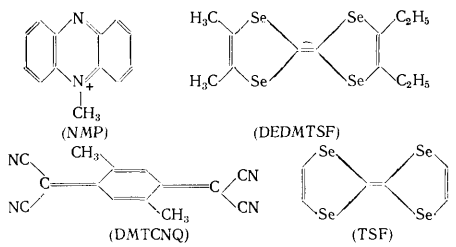
The structure of the CTC depends significantly on the Coulombic electrostatic interaction, on the elucidation of the role of which numerous studies have been carried out[20-27]. The charge transfer in the formation of the CTC leads to a considerable increase of the electrostatic energy owing to the repulsion of the charges of the neighbouring molecules in the column. This energy decreases either owing to the formation of complex salts or as a result of incomplete charge transfer. The possibility then arises of a resonance electron transfer via a relay mechanism:

$$\text{—}A^-\text{—}A^0\text{—}A^-\text{—}A^0\text{—} \rightarrow \text{—}A^0\text{—}A^-\text{—}A^0\text{—}A^-\text{—} .$$

In the tetrathiofulvalene—tetracyanoquinodimethane (TTF–TCNQ) complex there is not only incomplete charge transfer but charge density waves (CDW) are generated with a wave vector $4k_F$ ($\hbar k_F$ is the Fermi-quasi-momentum)[20]. The instability as regards the formation of the CDW is the only type of instability occurring at finite temperatures in the one-dimensional chain of a quasi-one-dimensional conductor and is due to the Coulombic electrostatic interaction and the interaction between the electrons and phonons of the three-dimensional crystal[21]. On decrease of temperature, a phase transition takes place in systems of this kind to a state with CDW, accompanied by the distortion of the lattice with a period $(4k_F)^{-1}$. In an ordered state non-linear CDW excitations constitute solitions with a gap in the excitation spectrum. Analogous collective states of a one-dimensional electron gas, which can be interpreted as isolated or bound solitons, can conduct an electric current[22,23]. The dependence of the current transmitted by solitons on temperature is of the activated type. The soliton model has been discussed in connection with the attempt to interpret the electrical conductivity peak in the TTF–TCNQ crystals[24].

The interaction of a rarefied electron gas with a highly polarised background can lead to an effective electron—electron repulsion. There is then a possibility of the Wigner "crystallisation" of the electron gas either in the form of individual electrons or in the forms of pairs[25-27]. The presence of such a generalised lattice makes it possible to interpret the optical spectra of TCNQ salts and to explain the satellite reflections on X-ray diffraction patterns[28]. The structure arising in the TTF–TCNQ complex is of the antiferroelectric type.

In systems containing components with a low symmetry there is a possibility of instability due to orientation disorder. The symmetry of planar centrosymmetric molecules can decrease as far as C_S following the introduction of one of two substituents. Examples of such compounds are provided by the complexes NMP–TCNQ, DEDMTSF–TCNQ (contain only asymmetric cations), TSF–DMTCNQ (contains only asymmetric anion), and others†.



One of the alternative possibilities in the packing of asymmetric fragments in the column is orientationally disordered packing. The influence of such disorder on the instability of the Peierls type has been examined[29]. The breakdown of translational symmetry on orientational deformation merely modulates, in contrast to shear deformation, the local energy of the electron, leaving unchanged the transition integrals. The gap in the electronic spectrum is then absent and the Peierls transition does not arise. Allowance for the interaction of the electrons of the one-dimensional chain with the rotational vibrations of the organic molecules (librons) demonstrated the possibility of the existence of states with the so-called chiral charge density waves (CCDW). A lattice instability with a wave vector $\mathbf{Q}=4\mathbf{k}_F$ corresponds to these. The transition to the state with CCDW can account for the continuous variation of the superstructure period from a to $2a$ and then to $4a$ in the TTF–TCNQ crystals, which occurs in the range 54–38 K. The electron–libron interaction is also very significant in TSF–TCNQ and $(TTF)_7I_5$.[30]

† Notation: NMP = *N*-dimethylphenazinium ion; DEDMTSF = diethyldimethyltetraselenofulvalene; DMTCNQ = dimethyltetracyanoquinodimethane; TSF = tetraselenofulvalene.

The lattice instability of the quasi-one-dimensional crystals is due in the general case to two fundamentally different contributions-dimerisation of the Peierls type via electron–phonon interaction and spin-Peierls dimerisation due to the spin–lattice interaction. The two different contributions have been estimated[31] using the self-consistent field approximation. Intermediate values of the interelectron interaction constants for which the electronic states are still delocalised, i.e. $t \propto U$, were taken. Here t is the integral for the transition of an electron between two nearest electronic states and U is the energy of the interaction of two electrons at a single site. By virtue of the quadratic relation between the exchange integrals and the transition integrals ($J \propto t_2$), the spin–lattice interaction is more effective than the electron–lattice interaction for intermediate values of t/U and for this reason the spin-Peierls transition is more probable than the Peierls transition.

The radical-anion salt $K^+TCNQ^{-\cdot}$, which undergoes a phase transition at 396 K, formally satisfies this model. Here there is a change in the energy gap and a complex rearrangement of the one-dimensional chain takes place and is accompanied by a rearragement of the spin structure. For this reason $K^+TCNQ^{-\cdot}$ is a spin system which exhibits Peierls instability in the vicinity of Tp.[32]

Ideas about the spin-Peierls instability have been used[33] to account for two Konno anomalies in quasi-one-dimensional TCNQ salts with the wave vectors $\mathbf{k}_1 = \mathbf{b}^*\rho$ and $\mathbf{k}_2 = \mathbf{b}^*\rho/2$, where $\mathbf{b}^*$ is the inverse lattice vector along the chains and ρ is the number of conductivity electrons per molecule ($\rho < 1$). For $\rho = 1/2$, the anomaly with $\mathbf{k}_1$ is caused by the electron–phonon interaction in which pairs of molecules containing one electron are combined into diads. The anomaly with $\mathbf{k}_2$ corresponds to the Peierls transition, i.e. the transition to the antiferromagnetic state in which the electrons of neighbouring diads form singlet pairs (it is assumed that $T_1 > T_2$). The lattice period is then quadrupled.

Studies on the infrared spectra of conducting quasi-one-dimensional crystals of TCNQ salts, initiated by Kaplunov et al.[34] and Kondow and Sakata[35], revealed their fundamental difference from the spectra of other molecular crystals. A characteristic feature is the presence of a broad absorption band associated with intermolecular charge transfer along the TCNQ column, beginning on the high-frequency side in the visible part of the spectrum and embracing the low-frequency infrared region to a greater extent the higher the electrical conductivity of the complex. This band covers the region of the low-frequency intramolecular vibrations (IMV) of the TCNQ molecules. The observed spectrum is not a simple sum of the electronic and vibrational spectra and has a more complex form: anomalously broadened asymmetric lines correspond to the intramolecular vibrations of TCNQ and the polarised spectra of the single crystals contain lines corresponding to the IMV with A_g symmetry, i.e. to electrical dipolar transitions which are prohibited for an isolated molecule.

The important role of the interaction of the electron system with IMV in the interpretation of the electronic, kinetic processes in TCNQ crystals has been established in a number of theoretical studies[36–42]. Allowance for the interaction is also necessary, according to Epstein and Conwell[43], in the analysis of temperature variation of the electrical conductivity and the electron mobility in crystals of TCNQ salts. We may also note that the study of the interaction of electrons with high-frequency IMV in organic conducting crystals is of interest in connection with the problem of high-temperature super-conductivity via the phonon mechanism. The first determination of the electron–phonon interaction constants for TCNQ salts by analysing the infrared spectra of the $TEA(TCNQ)_2$ salt (TEA = tetraethylammonium) has been carried out by Belousov et al.[44]

On the basis of a phenomenological model the above workers[44] obtained a formula for the component of the dielectric constant tensor along the conducting filaments:

$$\varepsilon_{\parallel}(\omega) = \varepsilon_{\parallel}^{\infty}\left[1 + \frac{(\omega_{le}^2 - \omega_{tl}^2)}{\omega_{te}^2 - \omega^2 - ig_e\omega - \sum\limits_k \gamma_k^2/(\omega_k^2 - \omega^2 - ig_k\omega)}\right],$$

incorporating the background dielectric constant $\varepsilon_{\parallel}^{\infty}$, the longitudinal frequency ω_{le}, the intrinsic frequency ω_{tl} of a one-dimensional harmonic oscillator describing the electronic transition with a decay coefficient g_e, the frequency ω_k and the decay coefficient g_k of IMV of type k, and the interaction constant γ_k.

This formula describes effects associated with the frequency shift and the occurrence of forbidden transitions known for Fano resonance[45]. The optical conductivity $\sigma(\omega) = \omega \mathrm{Im}\varepsilon_{\parallel}(\omega)$ spectrum differs significantly from the sum of the electronic and vibrational spectra. The spectrum illustrated in Fig. 2 is a result of the interference of the electronic and vibrational states and corresponds to the antiresonance of a continuous spectrum with a set of discrete vibrational levels. For example, the ω_k vibration, located on the low-frequency slope of the electronic band is manifested by an asymmetric band (with a width much greater than g_k), beginning with a shallow minimum on the high-frequency side, at a frequency close to ω_k. The vibration

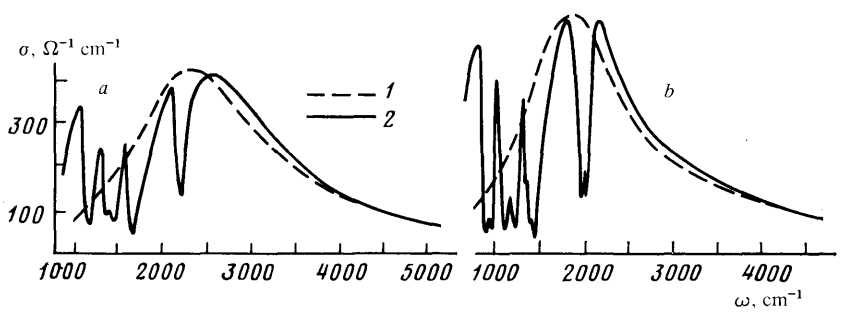


Figure 2. Spectroscopic relations for the optical conductivity of $TEA(TCNQ)_2$ crystals with E polarisation[44]: *1*) unperturbed electronic band; *2*) the same band with allowance for the interaction with intramolecular vibrations: *a*) 300 K; *b*) 100 K.

occurring in the region of the maximum of the electronic band is manifested by a "crossing-over point".

It has been shown[46] that the high dielectric constant of the salt TEA $(TCNQ)_2$ is due to the interaction of the low-frequency intramolecular TCNQ vibrations with electrons, leading to the formation of mixed electron–phonon states with a high oscillator strength.

The theoretical studies undertaken to elucidate the relation between the temperatures of the superconducting transition (T_c) and the Peierls transition (T_p) are important. It is known[47] that, to a first approximation, $T_c \cong T_p$ or the two temperatures are very similar, from which it follows that in such systems the superconductivity is fundamentally unobservable (the superconducting transition is suppressed by the dielectric transition). The two temperatures T_c and T_p increase monotonically with increase of the electron–phonon interaction constants and for low constants $T_c > T_p$, while for high constants, $T_c < T_p$.[48] This means that T_c for quasi-one-dimensional systems are hardly likely to be high, but they may nevertheless be appreciably higher than for a three-dimensional highly anisotropic metal[49]. Exciton shielding does not apparently exert a decisive influence on the electronic properties of radical-ion salts[50].

The problem of the influence of impurities in quasi-one-dimensional conductors on T_c and T_p has been studied[51,52]. For a weak electron–electron interaction, the impurities suppress the three-dimensional phase transition and increase the superconductivity fluctuation in unit chains. Marked scattering by the impurities fully suppresses the dielectric Peierls transition and, after the attainment of a certain critical concentration of impurities, the superconducting transition is also suppressed.

III. THE TETRATHIOFULVALENE–7,7,8,8-TETRACYANOQUINODIMETHANE COMPLEX

The attention of investigators has been mainly directed to a detailed study of the phase transitions in TTF–TCNQ crystals. Numerous precise measurements of the physical properties over a wide temperature range have now been carried out. The resistance R along conducting columns has been measured to within 10^{-5}. A sharp negative discrepancy at 53 K, associated with a second-order transition, has been observed in the relation between dR/dT and T.[53] The temperature dependence of the electrical conductivity in the range 20–300 K and at pressures up to 6×10^8 Pa exhibits two anomalies[54]. The temperature of the first (the metal–dielectric transition) (54 K and $p = 0$) increases with increasing pressure, while that of the second (38 K and $p = 0$) decreases slowly. Since the width of the conductivity band in the TTF–TCNQ complex increases with pressure in the experimental range of the latter, these results are difficult to interpret within the framework of the existing theory of the Peierls transition. The transitions have been interpreted[55] as independent transitions in the donor and acceptor columns, namely the transition at 54 K corresponds to ordering in the TCNQ chains while that at 38 K is associated with further ordering in the TTF chains, which leads to the appearance of a gap in the TTF column. Only one transition, at 29 K, is observed in TSF–TCNQ crystals, which can be accounted for by an intense interchain interaction.

The ability of the TTF–TCNQ and TSF–TCNQ complexes to form solid solutions makes it possible to obtain TTF_xTSF_{1-x}·TCNQ single crystals ($0 \leq x \leq 1$).[56–58]. Studies on the electrophysical properties of such crystals showed that the conductivity of the TTF–TCNQ crystal is determined by TCNQ chains in the range 300–58 K and by TTF chains in the range 58–38 K. The conductivities of the donor and acceptor columns in the TSF–TCNQ crystals are of the same order of magnitude. It therefore appears likely that both donor and acceptor columns are responsible for the transition at 38 K in TTF–TCNQ. The simple phase transition in TSF–TCNQ splits into two components after the addition of small amounts of TTF–TCNQ (<2%). The temperature of the high-temperature transition increases rapidly with increasing TTF concentration, while that of the low-temperature transition diminishes slowly, but the region of the anomaly in the resistance associated with this transition is markedly broadened.

Measurements of the velocity of sound in the range 0–300 K established[59,60] that Young's modulus is anistotropic ($E_a > E_b$, where b is the maximum conductivity axis), increases with decrease of temperature, and diminishes by several per cent in the vicinity of the transition point (54 K), the decay of sound at this temperature passing through a maximum. The increase of the velocity of sound by 1.5% at $T < 52$ K is due to the freezing of the conductivity electrons. A singularity is observed in the vicinity of T_p in the relation between the change in the magnetic susceptibility $d\chi/dT$ and T: $d\chi/dT \propto (T - T_p)^{1/3}$ and $\chi \propto \Delta^2$, where Δ is the width of the dielectric gap. There are no singularities on the $\chi(T)$ and $(d\chi/dT)(T)$ curves near the second transition[61], but they are manifested clearly on the $\chi(T)$ curve after the isolation of the contribution by the background (Fig. 3).[62]

Precise measurements of the heat capacity of the TTF–TCNQ crystals revealed four phase transitions, at 52.6, 48, 46, and 37 K,[63] while precise measurements of Young's modulus in the range 54–38 K led to the differentiation of five phase transitions[64]. These transitions can be regarded as martensite transformations in which the effects of the elastic interaction and of the ordering of microdomains, leading to one- and three-dimensional distortions of the lattice, play a significant role. The anomaly at 46 K is associated with a phase transition in the surface region, corresponding to the transition at 49 K in a massive specimen.

Measurements of neutron scattering in the range 38–54 K revealed the existence at $T < 38$ K of a three-dimensional structure with modulation of long-range order along the a and b axes in the initial monoclinic lattice with periods of $4a$ and $3.4b$.[65] The magnetoresistance of the TTF–TCNQ crystals $\Delta\rho/\rho = [\rho(50\text{ K}) - \rho(0)]/\rho(0)$ is smaller by 0.1% in the temperature range $T > 54$ K,[66] while at $T = 52.8$ K there is a magnetroresistance peak of 1.4%. The temperature T_p decreases in a magnetic field in accordance with the law

$$\Delta T \propto (\mu_B H)^2 (2k_F)^2 T_p$$

The results of Cooper et al.,[67] who investigated the influence of the isotope substitutions $^2H \rightarrow {}^1H$ and $^{15}N \rightarrow {}^{14}N$ on the transitions at 52.5 K (T_1) and 37.7 K (T_2), confirmed the view that the transitons in the TTF and TCNQ columns are independent. When both chains are deuterated, T_1 increases by 0.75 K, while the substitution of ^{14}N results in an increase by 0.6 K. When only TTF is deuterated, T_1 remains unchanged, but T_2 is altered. On the other hand, when only TCNQ is deuterated, T_1 increases by 0.7 K, while T_2 remains unchanged. This result can be explained by the fact that all molecular vibrations contribute to the Peierls instabilities; their relative contributions are determined by the binding constants. In TCNQ chains the instability is determined mainly by the intramolecular vibrations[68].

Several theoretical models have been proposed to account for the phase transitions in the range 38–54 K.[69–74]. The transitions at 54, 49, and 38 K can be accounted for on the basis of the Ginzburg–Landau theory. In contrast to the generally accepted interpretation, it has been claimed[73] that

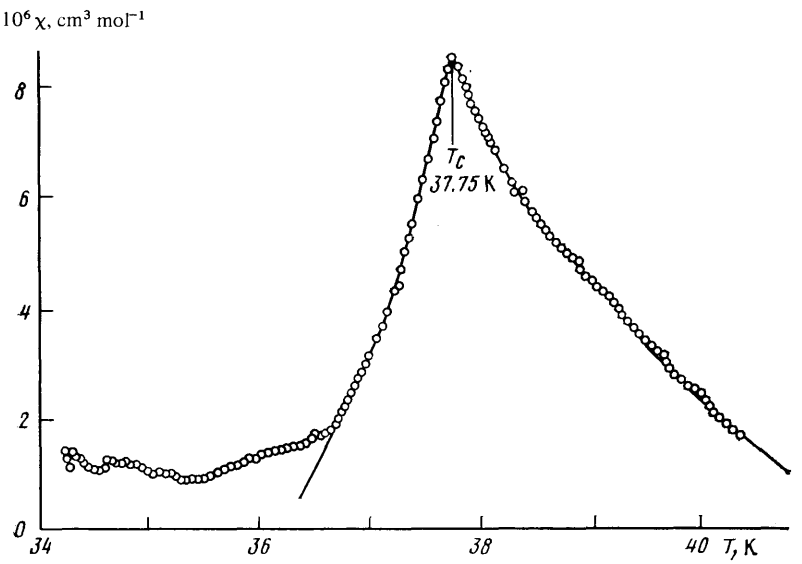


Figure 3. The anomaly in the magnetic susceptibility of the complex TTF–TCNQ near 38 K after the isolation of the background, giving rise to an exponential $\lambda(T)$ relation[62].

the transition at 54 K is associated with ordering in both filaments and not only in the TCNQ column. Experiments on X-ray scattering[72] made it possible to relate the transition at 54 K to the condensation of the anomaly with the wave vector $2\mathbf{k}_F$ in the form of the $2a \times 3.4b \times c$ superstructure, while the transition at 49 K can be related to the condensation of both longitudinal anomalies with the vectors $2\mathbf{k}_F$ and $4\mathbf{k}_F$.

In order to explain the microanomalies of Young's modulus in the range 38–52 K, a model based on the idea of the domain structure of the metallic and dielectric phases has been proposed[70]: it is believed that the column consists of conducting and non-conducting sections separated by domain walls consisting of a separate phase. The transition at 47 K corresponds to the formation of tetrads made up of metallic domains, while the transition at 38 K corresponds to their ordering. The transition at 34 K corresponds to the disappearance of metal–dielectric microdomain transitions from the TCNQ columns[70,71]. The transitions at 49–54 K have also been interpreted using the concept of phasons—excitations of the ground state with CDW which infringe the symmetry as a consequence of the phase shift of the CDW of the neighbouring chains[69]. The transition at 49 K corresponds to the instability of the phason mode. In this model there is a linear (in terms of the phason amplitude) interaction with a deformation of the crystal and the transition can therefore be suppressed by the application of an appropriate pressure. Thus, despite the abundance of experimental data, the theoretical interpretation of the results is not yet clear mainly due to the lack of a general theory of quasi-one-dimensional systems.

A series of detailed experimental studies have been made on the influence of the purity and perfection of TTF–TCNQ crystals on their electrophysical properties as well as the influence of the methods of measurement. One of the possible ways of taking into account the influence of the direction of the crystals is statistical analysis of the results of different workers. Such analysis, based on a survey of 600 measurements in 18 world laboratories[75], shows that the hypothesis of superconducting fluctuations is superfluous. The temperature T_P is in the range 54–58 K;[76] the scatter of the values is determined mainly by the degree of perfection of the single crystals and to a lesser extent by the concentration of the impurities.

This has been shown for TTF–TCNQ crystals with impurity concentration not exceeding 10^{-6}.[77,78] As a consequence of the low value of the disproportionation energy of the $TCNQ^-$ and TTF^+ radical-ions, the TTF–TCNQ crystals possess an internal source of contamination and, according to Haddon's data[79], the concentration of the impurities formed on disproportionation via the mechanisms

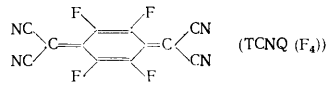
$$2TCNQ^{\cdot-} \rightarrow TCNQ^0 + TCNQ^{2-},$$
$$2TTF^{\cdot+} \rightarrow TTF^0 + TTF^{2+},$$

can reach 12%. Crystals grown from the gas phase are not free from such contamination either. This follows from the scatter of the values of σ_b (at 300 K) for such crystals, which are in the range $(2\text{–}6.7) \times 10^4\ \Omega^{-1}\ m^{-1}$.[80] A very great change in σ in the region of 58 K has not been observed either for large TTF–TCNQ crystals whose dimensions were $7 \times 0.5 \times 0.24$ mm and $30 \times 6 \times 0.7$ mm.[81] The concept of the anisotropy of σ arises from measurements of its principal values for a series of crystals: $\sigma_b = (4.40 \pm 0.15) \times 10^4$, $\sigma_a = (1.30 \pm 0.05) \times 10^2$, and $\sigma_c = (12.6 \pm 30.0) \times 10^2\ \Omega^{-1} m^{-1}$.[82] The scatter of the values of σ_c is due to the small thickness of the crystals in the direction of the c axis and the possible diffusion of the current-conducting silver paste through the crystal.

The magnitude of the transferred charge Δq in TTF–TCNQ crystals is important for the construction of a theoretical model for the latter. It has been determined by various methods and the scatter of its values proved to be small. Direct numerical integration in terms of X-ray structure factors yields $\Delta q = (8.55 \pm 0.95) \times 10^{-20}$ C.[83] Experiments on Raman scattering by TTF, TTF–TCNQ, and $(TTF)_7I_5$ crystals[84] in the temperature range 4–77 K yielded $\Delta q = 7.92 \times 10^{-20}$ C.[85] Two peaks of the $N1s$ levels have been observed

in the X-ray photoemission spectra, which corresponds to two TCNQ charge states (neutral and singly ionised)[86]. The ratio of the intensities of these peaks, proportional to Δq, yields the estimate $\Delta q \cong (8.87-10.61) \times 10^{-20}$ C.

Silverman[87] suggested that Δq for CTC is always smaller than unity, while for TTF–TCNQ it amounts to 9.35×10^{-20} C. All the results quoted above confirm the conclusion[88] that the optimum value of Δq, necessary for the preparation of highly conducting CTC, is $(9.50-12.67) \times 10^{-20}$ C per molecule. This is associated with two opposed factors: an increase of q entails an increase of the concentration of the conductivity electrons (and hence also of σ) and at the same time an increase of the Coulombic repulsion of the electrons, leading in the limit to the splitting of the conductivity band and the formation of localised electronic states. In fact, the value of Δq estimated by X-ray electronic spectroscopy for the TTF–TCNQ complex



(TCNQ (F_4))

with a low conductivity is $(15.04 \pm 3.17) \times 10^{-20}$ C.[89] A high value of Δq is obtained as a result of the high electron affinity (higher by 0.4 eV than that of TCNQ).[90] TCNQ(F_4) can therefore be used to obtain highly conducting CTC employing weaker donors.

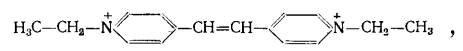
Complexes of TTF with TCNQ having a different stoichiometry are also known: $(TTF)_3(TCNQ)_2$ and $(TTF)_2TCNQ$.[91] These complexes are obtained by the low-temperature exchange method.

IV. CHARGE-TRANSFER COMPLEXES AND RADICAL-ION SALTS BASED ON 7,7,8,8-TETRACYANOQUINODIMETHANE

Simple radical-anion salts based on TCNQ have attracted the interest of both experimenters and theoreticians in connection with the fact that they exhibit two types of instability of the metallic state: the Mott and Peierls instabilities. In both of these salts a structural Peierls transition takes place at certain temperatures with retention of the Mott gap. Such a transition has been investigated[92] by X-ray diffraction for the salt Na^+TCNQ^-. In the low-temperature phase ($T < 353$ K) the distances in the $TCNQ^-$ column alternate: 3.212×10^{-10} and 3.429×10^{-10} m, while in the high-temperature phase all the distances are equalised: 3.385×10^{-10} m. The analogous transition at 396 K in K^+TCNQ^- crystals[93] is accompanied simultaneously by a rearrangement of the spin structure and K^+TCNQ^- is therefore a system which exhibits spin-Peierls instability in the vicinity of T_P. According to structural and magnetic data[94], the spin-Peierls instability is also characteristic of the violet ($T_P = 301$ K) and bluish-violet ($T_P = 215$ K) NH_4TCNQ^- phases.

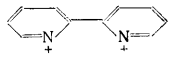
According to electrophysical measurements, heating results in phase transitions in TCNQ salts not only with alkali metals (Li, Na, and K) but also with transition metals (Mn, Fe, Co, Ni, Cu, and Zn).[95] The plot of $\lg \rho$ against $1/T$ in the range 300–500 K consists of two linear sections and of a transition region between them, the latter corresponding to a gradual accumulation of the high-temperature phase within the limits of the low-temperature phase, i.e. the transition is diffuse. In alkali metal salts of TCNQ these transitions have also been observed by infrared spectroscopy[96] from the sharp increase of the intensities of the lines corresponding to the vibrations of TCNQ molecules with A_g symmetry. The Coulombic interaction in these salts makes the main contribution to the dielectric gap, since at T_P the latter decreases insignificantly.

The report[97] of the preparation of the radical-ion salt $(DEPE)^{2+}(TCNQ)_4^{2-}$, where DEPE = bisdiethylpyridiniaethylene

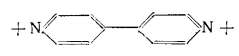


has aroused much interest among investigators. In this salt the metallic state persists up to ~0.03 K. The above communication led to a flood of publications[98-104] devoted to studies on this and similar radical-ion salts. Values of σ_{300} in the range $(1.5-22) \times 10^4\ \Omega^{-1}\ m^{-1}$ have been quoted in a number of studies[98,105,106] for the above radical-ion salt; $\sigma_{0.03}/\sigma_{300} \cong 3.7$. The thermo-e.m.f. is 35×10^{-6} V K^{-1} and is independent of temperature. However, according to Somoano et al.[99], σ_{300} of the monoclinic phase is $\sim 5 \times 10^3\ \Omega^{-1}\ m^{-1}$ and the $\sigma(T)$ relation is of the semiconducting type with an activation energy $E_a = 0.10 \times 10^{-19}$ J; the thermo-e.m.f. is saturated at high temperatures, reaching 6×10^{-5} V K^{-1}, which corresponds to a quarter-filled conductivity band. The erroneous nature of the conclusions reached in several studies[97,98,105,106] may be associated with the employment of thin $DEPE(TCNQ)_4$ single crystals, which might have resulted in the short-circuiting of the contacts owing to the diffusion of the current-conducting paste. Indeed, a semiconducting relation with $E_a = (0.32-0.48) \times 10^{-19}$ J has been obtained for a series of similar TCNQ salts[98-104], which were isolated in the form of larger crystals.

Interesting data concerning the influence of the symmetry of the cation on the electrophysical properties of the radical-ion TCNQ salts have been obtained[107]. The properties of the TCNQ radical-ion salts with symmetrical (4,4′-bipy) and asymmetric (2,2′-bipy) cations



(2,2′-bipy)



(4,4′-bipy)

are markedly different. The salt with the symmetrical cation is a semiconductor while that with the asymmetric cation is metal-like, in which the metal–dielectric transition occurs on cooling. The studies by Mihaly and coworkers[108,109] of the influence of the dipole moments of the donors are related to the above investigations. If the dipole moments are small, there is a possibility of a metallic state in which these moments are oriented at random. Scattering by the inhomogeneities of the electric field suppresses the dielectric transition and the salts behave as disordered metals. For large dipole moments, there is a possibility of the occurrence of an ordered charge state in which the salts behave as narrow-band conductors with a low conductivity.

The electrophysical properties of the TCNQ salt depends significantly also on the method of preparation (the specimens contain different amounts of $TCNQ^{2-}$ impurity ions). For example, a change in the concentration of the $TCNQ^{2-}$ ions in the salt $Qn(TCNQ)_2$ (Qn = quinolinium) alters E_a from 0.37 to 0.60×10^{-19} J, while σ is reduced by a factor of 10.[110] In addition, in the course of the preparation of the TCNQ salts, the molecules of many solvents can be incorporated in the crystal lattice of the complex; this usually decreases the resistance[111]. The influence of the solvent is manifested particularly effectively in the complex $(NMeQn)(TCNQ)_2$.[112, 113] A phase transition, accompanied by a sharp decrease of σ in the high-temperature phase occurs in this complex at 390 K. The transition is due to the decrease of the content of acetonitrile in which the complex was obtained. Its evaporation increases the structural disorder in the conducting

phase. The acetonitrile molecules act as a shield preventing the interaction of neighbouring chains and stabilise the thermodynamically unstable phase.

An unusual metal–dielectric phase transition occurs on heating crystals of the salt DECA $(TCNQ)_2$ (DECA = diethylcyclohexylammonium[114]). It is an irreversible first-order transition in which the initial column, consisting of TCNQ tetrads, is converted into one consisting of diads in the high-temperature phase. Sharp anomalies are observed on curves for the temperature variation of χ and the specific heat $\rho(T)$ (Fig. 4). The temperature of the transition depends greatly on the pressure ($dp/dT \cong 16 \times 10^4$ kg m^{-2} K^{-1}).

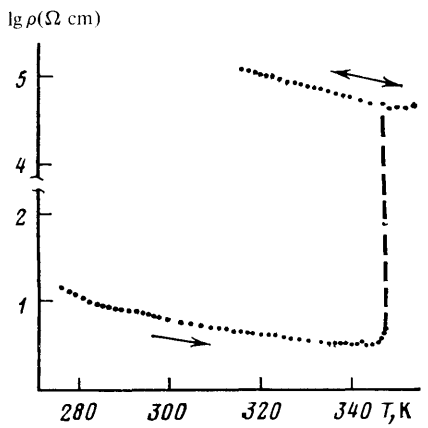


Figure 4. Temperature variation of the resistivity of DECA$(TCNQ)_2$ crystals[114].

When the salt $(NMe_3H)TCNQ$ was oxidised with iodine[115], a one-dimensional complex with a one-third filled band, having the composition $(NMe_3H)^+(I_3)^-_{1/3}(TCNQ)^{(2/3)-}$, was isolated. The anistropy of the electrical conductivity, measured by Montgomery's method, is ~400 and the conductivity $\sigma_{300} = 2000\ \Omega^{-1}\ m^{-1}$ increases up to 240 K, decreasing sharply at 160 K. The EPR line width decreases monotonically up to 160 K, after which it increases sharply. This transition is reversible and, according to the data of Delhaes et al.[116], is a Peierls transition.

Complexes formed by derivatives of dipyranylidene and its dithio-analogue, isoelectric with TTF, are of interest[117,118]. Such donors have low ionisation potentials and high polarisability. In particular, tetraphenyldiphyranylidene



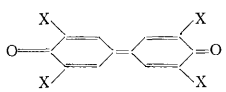
and tetraphenyldithiodipyranylidene form complexes with TCNQ; the conductivity of the first complex $\sigma_{300} \cong (2.4–4.0) \times 10^3\ \Omega^{-1}\ m^{-1}$ and decreases with decrease of temperature in accordance with an activation law ($E_a = 6.41 \times 10^{-21}$ J); the conductivity of the second complex $\sigma_{300} \cong (2.5–3.0) \times 10^4\ \Omega^{-1}\ m^{-1}$ and increases with decrease of temperature up to 145 K; below this temperature, the dielectric phase is stable. A reversible phase transition, in which σ decreases by two orders of magnitude, has also been observed in the tetraphenyldipyranylidene complex.

V. ORGANIC CONDUCTORS BASED ON CHARGE-TRANSFER COMPLEXES

Highly conducting compounds based on CTC were isolated as early as 1965 [119] using tetrathiotetracene (TTT) as the donor. *o*-Chloranil (*o*-CA), *o*-bromanil (*o*-BA), and tetracyanoethylene (TCNE) form complexes with the compositions $(TTT)_3$(*o*-CA), $(TTT)_3$(*o*-BA), and $(TTT)_3(TCNE)_2$. The resistances of the powdered specimens vary in accordance with an activation law ($E_a \cong 1.6 \times 10^{-20}$ J) and have the following values at 300 K:

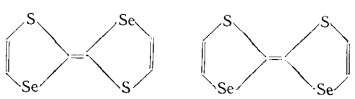
Acceptor	*o*-CA	*o*-BA	TCNE
$10^2\rho_{300}$, Ωm	2.4	6—8	15

Tetrahalogenodiphenoquinones have high electron affinities:

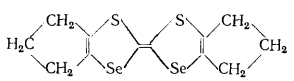


In particular 4.49×10^{-19} J, which is identical with the electron affinity of TCNQ, has been obtained for TCDQ and TBDQ.[90] The quinonoid structures of these complexes suggest a high polarisability. A series of TCDQ and TBDQ radical-ion salts have been described[120,121]. Salts containing cations, such as that of *p*-phenylenediamine (a Wurster radical-cation), ferrocenium, and cobaltocenium (0.2–0.8 Ωm, pelletted specimens) have low resistivities. Highly conducting complexes $TTT(TCDQ)_2$ and $TTT(TBDQ)_2$ are also formed by tetrathiotetracene[122] ($\sigma_{300} \cong 1.7$ and 8 Ω^{-1} m^{-1} respectively). It follows from infrared spectra that these complexes are radical-ion salts. Unfortunately, as a consequence of the extremely limited solubility of the RIS based on TCDQ and TBDQ, it is virtually impossible to isolate the salts in the form of single crystals.

Complexes of substituted derivatives and analogues of TTF with TCNQ and its derivatives have now been investigated in detail. As a rule, the weak asymmetry of the donor or acceptor stabilises the metallic phase of the complex, in which the latter behaves as a disordered metal. For example, mixed *cis–trans*-diselenodithiofulvalene (DSDTF)

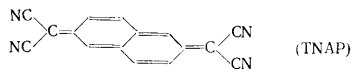


forms with TCNQ a complex having $\sigma_{300} = (7 \pm 3) \times 10^4\ \Omega^{-1}\ m^{-1}$, [123] which behaves as a disordered metal. Its dicyclopentano-derivative



(HMDSDTF)

forms with TCNQ and TNAP (11,11',12,12'-tetracyanonaphtho-2,6-quinodimethane)



(TNAP)

highly conducting RIS with the 1:1 composition ($\sigma_{300} \cong 10^4\ \Omega^{-1}\ m^{-1}$). [124] The complex of TMTTF (tetramethyltetrathiofulvalene) with 2,5-dimethyl-TCNQ has the conductivity $\sigma_{300} \cong 5 \times 10^4\ \Omega^{-1}\ m^{-1}$ with a sharp maximum at 50 K ($\sigma_{50}/\sigma_{300} = 10$) followed by the transition to the dielectric phase[125]. The addition of MTCNQ (methyl-TCNQ) to the complex TSF–TCNQ gives rise to the mixed complex $TSF(TCNQ)_{1-x}$-$(MTCNQ)_x$,

whereupon the peak in the $\sigma(T)$ relation shifts towards higher temperatures (from 40 to 75 K) and the gap in the electronic excitation spectrum in the region below the transition temperature diminishes so much that $\sigma_{4.2}$ for the mixed complex exceeds $\sigma_{4.2}$ for the initial complex by a factor of 10^4 (Fig.5). The complexes of TTF with 2,5-diethyl-TCNQ and 2,5-dimethyl-TCNQ are also disordered conductors, but the Peierls transition occurs at higher temperatures ($Tp \cong 180$–210 K) and the increase in σ amounts to only 50 and 20% respectively[125] (Fig.6). According to thermo-e.m.f. measurements the isostructural series of the CTC of TCNQ with TTF and *cis-trans*-DSDTF exhibits the properties of semiconductors at high temperatures, while in the range 40–60 K there is a transition to the dielectric phase[127]. For example, the conductivity maximum in DSDTF–TCNQ crystals is observed at 60 K.[128] The complexes# of OMTTF, OMDSDTF, DBTTF, and DBDSDTF with TCNQ and TNAP are dielectrics[124,129]. Possibly the reason for this is the appreciable difference from the planar structure of the dicyclohexano-derivatives, on the one hand, and the high ionisation potentials of the dibenzo-derivatives, on the other.

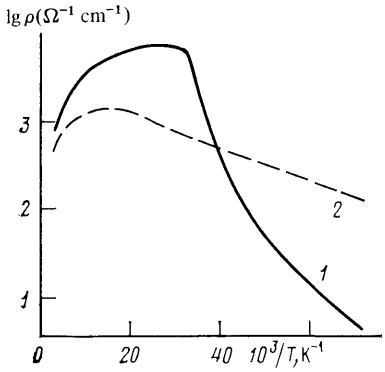
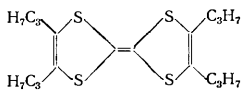


Figure 5. The electrical conductivity of TSF–TCNQ (curve *1*) and $TSF(TCNQ)_x(MTCNQ)_{1-x}$ (curve *2*) crystals[126].

Similarly the complex of the tetrapropyl derivative of TTF with TCNQ



(TPTTF)

is a dielectric having a structure of the interleaved type[130], while the magnetic and dynamic properties of the complex TMTTF–TCNQ (TMTTF = tetramethyl-TTF) are similar to those of TTF–TCNQ.[131] Apparently the main reason for this is the presence of a bulky substituent and hence an insufficiently effective overlap in the column consisting of TPTTF molecules alone.

#Notation: OMTTF = octamethylene-TTF, OMDSDTF = octamethylene-DSDTF, DBTTF = dibenzo-TTF, DBDSDTF = dibenzo-DSDTF, TNAP = tetracyanonaphthoquinodimethane, and HMTTF = hexamethylene-TTF.

However, the complex HMTTF–TCNQ (it contains a non-planar cation) exhibits a metallic type of conductivity up to ~75 K, after which it is converted into the dielectric phase[132]. The two sharp transitions at 49 ± 1 and 43 ± 1 K have been related to the rearrangement of the HMTTF and TCNQ columns respectively. Furthermore, the complex HMTSF–TCNQ (where HMTSF = hexamethyltetraselenofulvalene) retains the metallic type of conductivity up to 0.06 K. Apparently the deviations from the planar structure of these donors are not sufficiently significant to prevent an effective overlap of the donor orbitals in the column. The interaction between the HMTSF and TCNQ columns, manifested by short-circuited intermolecular contacts, has also been observed in the complex HMTSF–TCNQ.[133] In all probability this effect stabilises the metallic phase. Measurements of the anisotropy of the conductivity of organic semiconductors[134] (see Table) have shown, however, that the HMTSF–TCNQ crystal is far from being isotropic. To some extent, it can be regarded as an anisotropic quasi-two-dimensional conductor formed by layers oriented along the *a* and *b* axes.

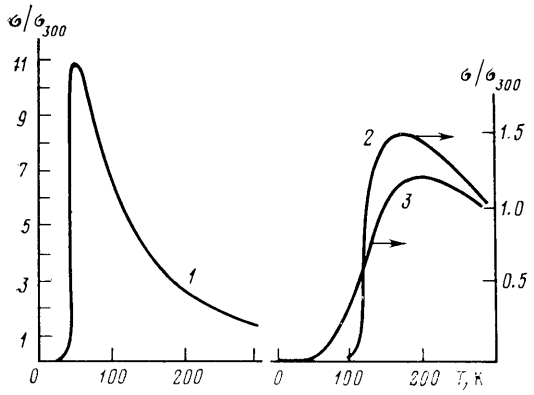


Figure 6. Temperature variation of the electrical conductivity of CTC containing low-symmetry acceptors: *1*) TMTSF–DMTCNQ; *2*) TTF-DETCNQ: *3*) TTF–MTCNQ.[125]

The anisotropy of the conductivity of organic conductors at 300 K.

Conductor	σ_b/σ_a	σ_b/σ_c	$10^4\sigma_{b_{300}}$ Ω⁻¹ m⁻¹
TTF—TCNQ	300—500	120	4±1
TSF—TCNQ	150—300	130—280	8±1
HMTSF—TCNQ	30	450	18±2

The high anisotropy of the conductivity of the complexes TMTSF–TCNQ, TMTTF–TCNQ, and DEDMTSF–TCNQ has been observed by Andersen[135]. In interpreting these results, one may conclude that, in compounds containing sulphur, the current flows via both donor and acceptor columns, while in compounds containing selenium it flows only via acceptor columns. Two phases—conducting and dielectric—are known for the complex TMTSF–TCNQ.[136]

In general, polymorphism is a very common phenomenon for CTC. Polymorphism is possible for identical compositions and can be due to different contents of the solvent. Polymorphism of type P_1 is known for NMP–TCNQ, Et_2TCl. $.(TCNQ)_2$ (Et_2TCl = 3,3′-diethylthiazolinecarbocyaninium ion), RbTCNQ, TMPD–CA, and K^+CA^-.[137] The two forms can crystallise simultaneously; they can be frequently distinguished even visually and in other cases a difference is observed when the optical or electrophysical properties are investigated.

The incorporation of solvent molecules in the CTC lattice (P_2 polymorphism, i.e. polymorphism of the second kind) can alter markedly the physical property of the complex. The complex $TTT(TCNQ)_2$ incorporates acetonitrile, chlorobenzene, or nitrobenzene molecules, which leads to a highly disordered structure. The complex benzidine–TCNQ incorporates methylene chloride or benzene.

Cooling of K^+CA^- crystals, containing a one-dimensional chain of radical-ions CA^-, leads to a phase transition, which is clearly manifested on the $\chi(T)$ curve (Fig.7).[138] The susceptibility of the low-temperature phase is described equally satisfactorily by the singlet–triplet excitation model and the Ising model. The hydrated form of the salt is diamagnetic in the range 70–300 K, which is associated with the stabilisation of the singlet ground state (in the hydrated form the CA^- chain consists of singlet dimers).

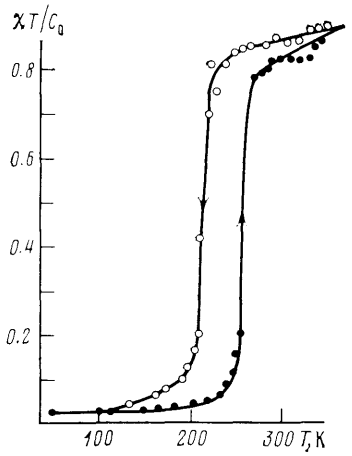
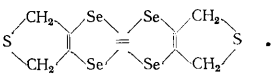


Figure 7. Temperature variation of the magnetic susceptibility of K^+CA^- crystals; $\chi T/C_0$ = dimensionless parameter; C_0 = Curie constant.

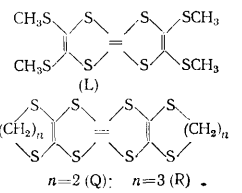
An idea about the influence of the nature of the donor on the electrophysical properties of the CTC is provided by the temperature Tp determined[139] from measurements of the dielectric susceptibility:

CTC	TTF–TCNQ	DSDTS–TCNQ	TSF–TCNQ	$TTF_{0.97}TSF_{0.03}TCNQ$	TMTTF–TCNQ
T_P, K	53	50	29	50	40

The metallic phase becomes more stable both on replacement of sulphur by selenium and after the introduction of a substituent with a small bulk. In both cases the intermolecular contacts between the donor and acceptor columns are improved. A series of donors, which are analogues of TTF but are superior to the latter as regards their electron-donating capacity, have been synthesised; for example, di-2,5-dihydrothieno-1,4,5,8-tetraselenofulvalene is structurally similar to HMTSF:[140]



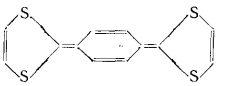
It forms a 1:1 complex with TCNQ, whose conductivity $\sigma_{300} = 6 \times 10^4\ \Omega^{-1}\ m^{-1}$. A series of TTF derivatives with a still higher sulphur content, namely alkylthioderivatives, have been obtained:



(L)

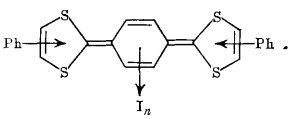
n=2 (Q); n=3 (R).

These donors form with TCNQ CTC having the composition L(Q,R)TCNQ in the form of black crystals. The conductivities σ_{300} of the complexes Q–TCNQ and R–TCNQ are higher than that of TTF–TCNQ, while σ_{300} for L–TCNQ is lower[141]. Finally the derivative of a superdonor, namely tetrathioquinodimethane



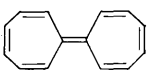
(TTQ)

was isolated in the form of diphenyl-TTQ iodide:



This iodide exists in the form of an equilibrium mixture of the RIS and the CTC.[142] The neutral TTQ has been obtained only in the form of a red solution in benzene which is extremely unstable as regards oxidation.

The study of the electronic absorption spectra of solutions of heptafulvalene



and TCNQ showed that the application of this donor (isoelectronic with TTF) is promising for the synthesis on its basis of CTC and RIS.[143] Unfortunately the complex was not isolated from solution.

Thus the only CTC retaining metallic properties at helium temperatures is the complex HMTSF–TCNQ)conductivity of the metallic type is retained by this complex at pressures $p > 2.5 \times 10^8$ Pa and temperatures up to 2×10^{-2} K).[144] At low temperatures it exhibits a high and anisotropic magnetoresistance and a high mobility of carriers (~$4 \times 10^8\ m^2\ V^{-1}\ s^{-1}$ for electrons and $1.2 \times 10^8\ m^2\ V^{-1}\ s^{-1}$ for holes). The disappearance of magnetoresistance at temperatures above 80 K indicates the one-dimensional nature of the system at these temperatures. The magnetic susceptibility increases with temperature. A considerable Hall e.m.f. was observed for the first time for quasi-one-dimensional conductors in the complex HMTSF–TCNQ.[145,146] The possibility of this effect in quasi-one-dimensional conductors was predicted by Lyo[147]. In the two-band model of the CTC the Hall mobility is caused either by a jump mechanism (when the bands do not overlap) or by resonance tunnelling (overlapping or coinciding bands). The Hall constant R_H for HMTSF–TCNQ crystals is positive at

high temperatures, increases on cooling down to 50 K, and then changes sign at 32 K, which implies an increase of the contribution of electrons to conductivity compared with holes on cooling.

The Hall effect has also been observed in TTF–TCNQ crystals by means of d.c. measurements[148] and by the ultrahigh frequency method[149]. At room temperature the value of R_H measured using a direct current is $-(4.2 \pm 0.6) \times 10^{-5}$ V Wb^{-1} m^{-1}, which agrees with the conclusion[55] that the acceptor columns make a dominant contribution to the electrical conductivity of the complex TTF–TCNQ.

VI. ORGANIC CONDUCTORS BASED ON RADICAL-CATION SALTS

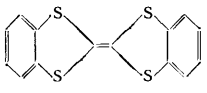
Conductors based on radical-cation salts with simple, mainly inorganic anions possess hole type conductivity. At the present time such conductors have been obtained from derivatives and analogues of TTF, TTT (tetrathiotetracene), and TST (tetraselenotetracene). Their composition can be expressed by the formula DY_n (where D = TTF, TTT, or TST and Y is an inorganic anion), n being as a rule non-integral.

The methods of synthesis of the radical-cation salts have been discussed in a review[17]. The halides are frequently obtained by the direct oxidation of solutions of donors by solutions of the corresponding halogens. The donor : halogen ratio, which can be varied within wide limits, determines the composition of the salts.

Direct oxidation of TTF with iodine and bromine yields salts having the composition $TTF(I)_{0.71}$ and $TTF(Br)_{0.71}$.[150, 151] The conductivity of the bromide is (300–350) $\times$ 10^2 Ω^{-1} m^{-1}, changes little in the range 180–300 K, and rapidly decreases below 180 K with an activation energy of 0.13×10^{-19} J. The electrical conductivity of the iodide crystals is $\sigma_{293} = (1.0–4.5) \times 10^4$ Ω^{-1} m^{-1} and diminishes sharply at 240 K, exhibiting a considerable hysteresis. In the region of the transition there are anomalies both in the thermo-e.m.f. and in the intensity of the EPR lines. All these features are associated with a strong interaction of the one-dimensional chains in the salt crystals and also with the change in the interaction of iodine with the TTF columns in the region of the metal–dielectric transition[152].

The thiocyanates of those donors whose composition depends on the initial reactant ratio and the structure of the donors have been obtained by the direct oxidation of TTF and TMTTF by solutions of dithiocyanogen $(SCN)_2$: TTF forms the salts $TTF(CNS)_{0.5}$ and TTF(SCN), while TMTTF gives rise to salts with the compositions TMTTF.$(SCN)_{0.5}$ and TMTTF$(SCN)_2$ (the latter is a dielectric[153]). When the donor : halogen ratio was varied in the range from 1 : 0.5 to 1 : 8, a series of TMTTF salts with the following compositions were obtained: $(TMTTF)I_n$ (n = 0.5, 1.3, 2.6, and 3.7) and $(TMTTF)Br_n$ (n = 0.5, 0.8, and 6.0).[154]

A series of radical-ion salts have been obtained by oxidising TTF with copper(II) chloride and the composition of these salts depends on the nature of the solvent. The purple complex $(TTF)_3(CuCl_2)_5$, containing $TTF^{\ddagger}$ and TTF^{2+}, was isolated from ethanol[155]. After recrystallising from acetonitrile, a black acicular salt $(TTF)_2CuCl_4$ is obtained, while direct oxidation in acetonitrile yields the yellow product $TTF^{2+}(CuCl_4)^{2-}$.[155] A series of organic conductors based on dibenzotetrathiofulvalene



(DBTTF)

have been isolated on oxidation of the latter with metal salts. In particular, the salts $D(SnCl_6)_{0.375}$, $D_4Ti_2Cl_9$, $D_8Pt_2Cl_9$, D_2PtCl_5, $D_7Pt_2Br_9$, $DPtBr_5$, D_2FeCl_4, $DFeCl_4$, $D(PtCl_6)_{0.375}$, $D(SnCl_6)_{0.375}$, and $D_{2.5}FeCl_4$ (here D = DBTTF) were obtained[156–159]. The salts $D(MCl_6)_{0.375}$ (M = Pt or Sn) and $D_{2.5}FeCl_4$ are conductors, passing to the state of a Peierls dielectric at 180–200 K. They contain DBTTF with a formal degree of oxidation of 0.75–0.8, which is most favourable for the occurrence of the metallic state[88].

The method of synthesis of radical-cation salts by an exchange raction is effective in many instances. For example, the thio- and seleno-cyanates of TTF having the compositions $(TTF)_{11}Y_6$ (Y = SCN or SeCN)[160,161] and $(TTF)_7I_5$ have been isolated. They are all isomorphous, but the iodide is a semiconductor, while the thio- and seleno-cyanates are conductors up to 220 K. Somoano et al.[162] quoted a different composition of the thio- and seleno-cyanates, namely $(TTF)_{12}Y_7$. The thermo-e.m.f. of these salts is positive and decreases linearly as the temperature is reduced, which confirms the metallic type of their conductivity and implies that the current carriers are holes.

One of the effective methods of synthesis of radical-cation salts involves oxidation with hydrogen peroxide in the presence of the corresponding acid. The oxidation of DBTTF in the presence of HBF_4 in benzonitrile yields the salt $DBTTF(BF_4)_{0.80}$.[163] The conductivity of compressed salt specimens ($\sigma_{300} \cong 80$ Ω^{-1} m^{-1}) changes little on cooling to 180 K, after which there is a sharp transition to the dielectric phase. The substance then remains in the paramagnetic phase and for this reason the transition can be due to Mott instability. TMTTF tetrafluoroborates have the compositions $TMTTF(BF_4)_{0.5}$ (conductor) and $(TMTTF)_x.(BF_4)_y$ ($x/y \cong 1$, dielectric, $\sigma_{300} \cong 2 \times 10^3$ Ω^{-1} m^{-1}).[164]

All the TTF halides contain a more or less large amount of impurities of internal origin due to the disproportionation of the $TTF^{\ddagger}$ radical-cation via the mechanism

$$2TTF^{\ddagger} \rightleftharpoons TTF^0 + TTF^{2+} \quad .$$

The random temperature-dependent distribution of impurities stabilises the metallic state[165].

The radical-cation salts of TTT and TST are perhaps of greatest interest at the present time. A whole series of TTT iodides, formed on direct oxidation of TTT with iodine, have been isolated. The iodide (TTT)I is a conductor up to 200 K, while the iodide $(TTT)I_{1.5}$ is a conductor up to 50 K.[166] Studies of the electronic spectra of the crystals and solutions of $(TTT)I_{1.5}$ showed that this salt is the tri-iodide $(TTT)_2^{+}I_3^{-}$,[167] i.e. the degree of oxidation of TTT in this substance is 0.5. The metal–dielectric transition in the salt $(TTT)_2I_3$ has not been observed[168] up to 3.3 K. At 50 K the quantity $\sigma(T)$ passed through a maximum, but the system remained in a conducting state. Subsequently the isolation of the iodide $(TTT)I_{1.6}$ [single crystals, $\sigma_{300} = (7.0–15.0)$ 10^4 Ω^{-1} m^{-1}] was reported[169]. The degree of disorder in this substance is such that the dielectric Peierls transition is suppressed. The situation was clarified after the publication of a study[170] in which it was shown that in reality one should consider the phase $(TTT)I_x$, where x varies from 1.5 to 1.55. With increase of x, the quantity I_{max} diminishes and σ_{max} is greater the smaller the value of T_{max}. At low temperatures there is nevertheless a metal–dielectric transition whose temperature depends significantly on the iodine content. The same workers described a new iodide $(TTT)I_3$ ($\sigma_{300} \cong 50$ Ω^{-1} m^{-1}).

Crystals of the iodide $(TTT)_2I_3$ can be obtained also in the gas phase[171,172], but its structure is not the same as that quoted by Buravov et al.[166] and $T_{max} = 35 \pm 3$ K. Interesting results have been obtained in the calculation of

the Madelung energy of the iodide $(TTT)_2I_3$.[173] Depending on the relative shift of the I_3 ions, this energy has two minima separated by a maximum with $E_a = 4.8 \times 10^{-20}$ J, which gives rise to the possibility of a relative slip of the ions in the $(I_3)_x$ chain with increase of temperature and this leads to structural disorder.

The joint oxidation of TTT with iodine and bromine makes it possible to isolate the mixed salt $(TTT)_2I_xBr_{3-x}$.[174] Qualitatively the $\sigma(T)$ relation is similar to that observed for the pure iodide, but T_{max} is higher, amounting to 150–180 K.

Khidekel' and coworkers[175] obtained TST iodides having the compositions $(TST)I_{0.7-0.8}$, $(TST)I_{1.80-1.85}$, and $(TST)I_{2.2-2.4}$ and an iodide of unknown composition $(TST)I_x$. Khidekel' and Yagubskii and coworkers[176,177] described TST chloride and bromide having the compositions $(TST)_2X$ (X = Cl, Br, or CSN). They are obtained when TST is oxidised by one-electron oxidants (TCNQ, TCNE) in the presence of Cl^-, Br^-, or CSN^- ions. The chloride and bromide are conductors, while the thiocyanate is a semiconductor. Subsequent studies in Shchegolev's laboratory[178,179] on $(TST)_2Cl$ crystals led to the discovery of a phase transition at 25 K of the metal (I)–metal (II) type and of a high-pressure phase at $p > 6 \times 10^8$ Pa, which is also of the metallic type [metal (III), $\rho_{10K} \cong 1.1 \times 10^{-7}$ Ω m]. According to a remark by Shibaeva and Kominskii[133], a common feature of the structures of the complexes (HMTSF)TCNQ and $(TST)_2Cl$ is the interaction between the columns manifested by shortened intermolecular contacts.

The study of the magnetoresistance and the anisotropy of the conductivity of $(TST)_2Cl$ [180] leads to the analogous conclusion, namely that, although, the low-temperature state is strongly anisotropic, its anisotropy is not uniform.

VII. CONDUCTORS BASED ON ORGANOMETALLIC AND COORDINATION COMPOUNDS

Mixed valence platinum complexes have already become traditional objects of study. Apart from the thoroughly investigated platinum cyanide, partly oxidised with chlorine or bromine, highly conducting compounds based on complex oxalates have also been isolated. At the same time conductivity of the metallic type have also been observed, for example, in the compounds $(H_3O)_{1.6}[Pt(C_2O_4)_2]_n.H_2O$ [181] and $K_{1.6}[Pt(C_2O_4)_2].1.2H_2O$; the latter contains, like the complex cyanide $K_{1.75}[Pt(CN)_4].1.5H_2O$ [182,183], a quasi-one-dimensional zig-zag chain of platinum atoms in which there are three crystallographically non-equivalent platinum atoms (Fig. 8). The groups $Pt(C_2O_4)_2$, located at a distance $c/2$, are in the eclipsed configuration and those at a distance $c/4$ are in the staggered configuration. Analogues of the Krogmann salt, namely $(NH_4)_2[Pt(CN)_4]Cl_{0.3}3.2H_2O$ and $(NH_4)_{2.2}.[Pt(CN)_4]Cl_{0.5}.3H_2O$, in which the dielectric Peierls transition occurs at 150 K,[184] and the salt $[C(NH_2)_3]_2[Pt(CN)_4].Br_{0.23}.H_2O$, which exists in the state of a Peierls dielectric even at room temperature[185], have been obtained by exchange reactions. The soliton conduction mechanism is possible for the last salt.

The electrochemical oxidation of the salts $M_2[Pt(CN)_4]$ in the presence of F^- or HF_2^- ions led to the isolation of the following salts from aqueous solutions:

$$K_2[Pt(CN)_4](HF_2)_{0.30} \cdot 3H_2O \ (I), \quad Rb_2[Pt(CN)_4](HF_2)_{0.40} \ (II),$$
$$Rb_2[Pt(CN)_4](HF_2)_{0.26} \cdot 1.7H_2O \ (III), \quad Cs_2[Pt(CN)_4](HF_2)_{0.39} \ (IV),$$
$$Cs_2[Pt(CN)_4](HF_2)_{0.23} \ (V), \quad [C(NH_2)_3]_2[Pt(CN_4)](HF_2)_{0.26} \cdot H_2O \ (VI).$$

The conductivities of salts (II), (IV), and (V), measured on single crystals at room temperature, are respectively 1.6×10^5, 2×10^5, and $(2.5–3.5) \times 10^4$ Ω^{-1} m^{-1}.[186,187] The temperature dependence of the conductivities of certain platinum complexes is illustrated in Fig. 9.

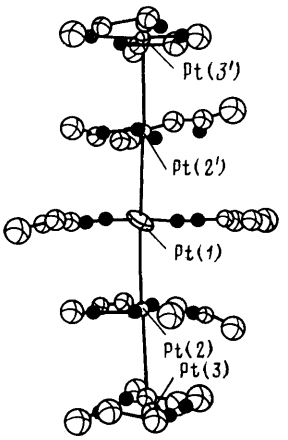


Figure 8. One-dimensional chain of $[Pt(C_2O_4)_2]^{1.6-}$ ions containing three crystallographically non-equivalent Pt atoms[182].

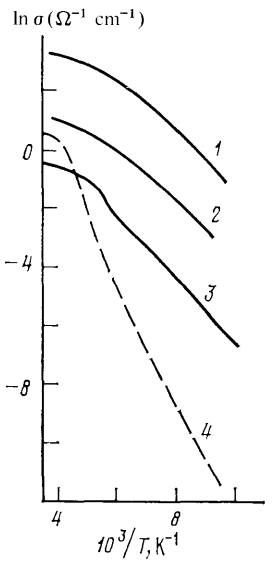


Figure 9. Temperature variation of the electrical conductivity of crystals of complex platinum cyanides: *1*) $K_2[Pt.(CN)_4Cl_{0.3}.3.2H_2O$; *3*) $(NH_4)_2[Pt(CN)_4Cl_{0.3}.3.2H_2O$; *4*) $(NH_4)_{2.2}[Pt(CN)_4]Cl_{0.5}.3H_2O$.[184]

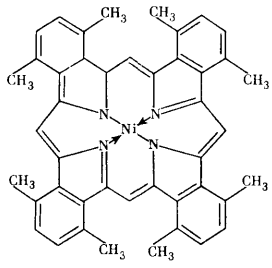
Partially oxidised phthalocyanines and porphyrins form a new class of highly conducting quasi-one-dimensional organic metallic compounds[17,188–191]. Such compounds are obtained, for example, on partial oxidation with iodine of

transition metal (Fe, Co, Ni, Cu, Zn, Pt) complexes of phthalocyanine (Pc):

$$MPc + \frac{x}{2} I_2 \rightleftharpoons (MPc) I_x \quad .$$

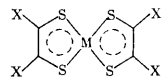
The iodine is present in these compounds mainly in the form of the ion I_3^-; $0.5 \leqslant x \leqslant 3.0$. The conductivity of some of these compounds ($CuPcI_{1.71}$ and $PtPcI_{0.93}$) is comparable to that of the complex $Qn(TCNO)_2$.

The resistance of thin PbPc films decreases with decrease of temperature down to 50 K and remains constant at lower temperatures. Hence the conductivity of porphyrins partly oxidised with iodine increases slightly as the temperature is reduced from 380 to 300 K. After the oxidation of the nickel complex of 1,4,5,8,9,12,13,16-octamethylenetetrabenzoporphyrin, i.e. Ni(OMTBP)



with iodine, the compounds $Ni(OMTBP)(I_3)_y$ with $y = 0.35 \pm 0.03$ and 0.97 ± 0.10 were isolated. The conductivity of the complex with $y = 0.35$ has a maximum at $T \cong 300$ K [$\sigma_{max} = 1.5 \times 10^3\ \Omega^{-1}\ m^{-1}$ (Fig.10)], while for the complex with $y = 0.97$ the maximum is displaced to $T = 340$ K.

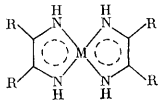
Another interesting class of organometallic compounds forming crystals with a quasi-one-dimensional structure consists of transition metal olefindithiolates with the general formula $M(ODT)_2$ (ODT = olefindithiolate ion having a planar structure with D_{2h} symmetry):



Here M is a transition metal atom and x = alkyl, aryl, CN, CF_3, or H. A characteristic feature of the olefindithiolates is the ease of their one- and two-electron reduction with retention of the planar structure:

$$M(ODT)_2 \overset{+e}{\underset{-e}{\rightleftharpoons}} M(ODT)_2^- \overset{+e}{\underset{-e}{\rightleftharpoons}} M(ODT)_2^{2-} \quad .$$

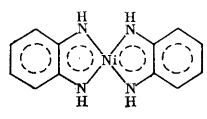
Similar properties are characteristic also of transition metal olefin di-iminates of the same composition:



Five degrees of oxidation are known, for example, for nickel o-phenylene di-iminate:

$$Ni(Pda)^{2+} \overset{+e}{\underset{-e}{\rightleftharpoons}} Ni(Pda)^{+} \overset{+e}{\underset{-e}{\rightleftharpoons}} Ni(Pda) \overset{+e}{\underset{-e}{\rightleftharpoons}} Ni(Pda)^{-} \overset{+e}{\underset{-e}{\rightleftharpoons}} Ni(Pda)^{2-}$$

Ni(Pda) =



All its forms have a planar structure[192].

The use of olefindithiolates and olefin di-iminates for the synthesis of CTC and RIS based on them is doubly interesting, since there is a possibility, in principle, of the formation in such compounds of conducting acceptor or donor columns by the overlap of the d_{z^2} orbitals of the transition metal partly filled as a result of charge transfer. In this sense, they can combine the properties of the mixed valence platinum cyanides (radical-cation salts) and CTC based on TCNQ or TTF.

Some of the complexes of this type which have been isolated do indeed exhibit a high conductivity. For example perylene (PE) forms conducting complexes with nickel, copper, and palladium maleodinitriledithiolates (mnt) having the composition $(Pe)_2^+[M(mnt)_2]^-$ and a thermally activated conducting state [$E_a \cong (1.6\text{–}3.2) \times 10^{-21}$ J].[193] According to Bray and coworkers[194,195], the complex $(TTT)_{1.2}NiS_4C_4H_4$, isolated in the form of black crystals ($\sigma_{298} \cong 3 \times 10^3\ \Omega^{-1}\ m^{-1}$) is a quasi-one-dimensional conductor. Its crystals are formed by one-dimensional TTT chains separated by $[NiS_4C_4H_4]^-$ ions. The degree of filling of the electronic band in this substance is 1/6. The activated nature of the conductivity of the complex ($E_a \cong 1.76 \times 10^{-20}$ J) is due to the presence of the Peierls gap. The electronic and magnetic properties are fully analogous to those of a radical-cation salt.

The complex $(TTF)_2NiS_4C_4H_4$ has been isolated. The complexes of TTF with olefindithiolates have interesting magnetic properties. The magnetic susceptibility of the complexes $TTF[PtS_4C_4(CF_3)_4]$ and $TTF[NiS_4C_4(CF_3)_4]$[196,197] is described by a model consisting of a one-dimensional ferromagnetic with antiferromagnetic interaction between the chains. The peak in the $\chi(T)$ relation at a temperature below 12 K corresponds to the antiferromagnetic ordering. The complex $(TTF)_2[NiS_4C_4H_4]$ is a paramagnetic with single unpaired electrons per molecule.

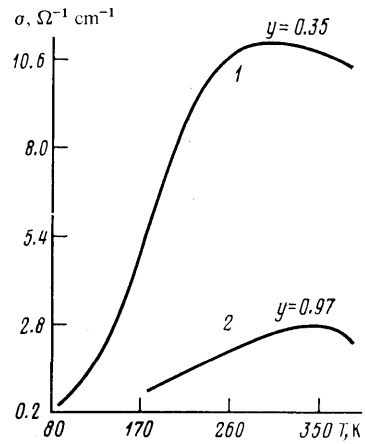
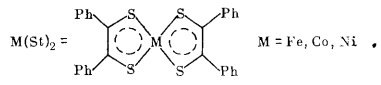


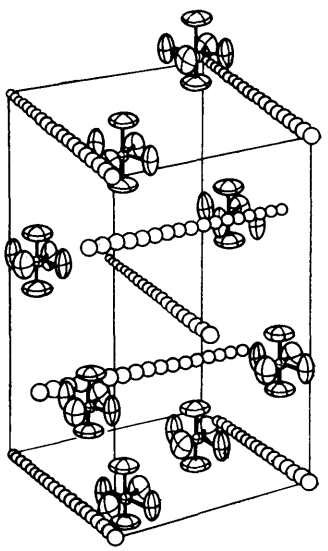
Figure 10. The conductivity of $Ni(OMTBP)(I_3)_y$ crystals: *1*) $y = 0.35$; *2*) $y = 0.97$.[191]

The possibility of the replacement of the central atom in the molecules of olefindithiolates makes it possible to vary their magnetic properties within wide limits. This has been demonstrated in relation to transition metal stilbenedithiolates[198],



Nickel stilbenedithiolate is a diamagnetic; the Curie-Weiss law is valid for the susceptibility of $Co(St)_2$ in the range 4–300 K ($\Theta < 1$ K, $\mu_{eff} = 2.06\ \mu_B$), while the susceptibility of the complex $Fe(St)_2$ is described by a model consisting of a one-dimensional Heisenberg antiferromagnetic with a low-temperature increase of $\chi(T)$ due to the finite chain length[198].

The study of the magnetic properties of the complexes $TTF[MS_4C_4(CF_3)_4]$ (M = Cu or Au) led to the discovery of a fundamentally new phenomenon—the spin-Peierls transition[199–201], theoretically predicted by Pytte[202]. The susceptibilities of both complexes have a broad maximum at $T \approx 50$ K; for $T = 12$ K (M = Cu) and 2.1 K (M = Au), the quantity $\chi(T)$ diminishes smoothly. This decrease is described satisfactorily by the theory of the one-dimensional Peierls transition in an antiferromagnetic Peierls chain. At $T < Tp$ new crystalline phases of the complexes contain paired TTF groups with a spin $S = 1/2$.



○ Hg atom ⊕ As atom ⊕ F atom

Figure 11. The crystal structure of $Hg_{2.86}AsF_6$.

Perhaps the most interesting properties among inorganic highly anisotropic compounds are shown by mixed-valence mercury salts[203–210]. In liquid sulphur dioxide direct interaction of mercury with stoichiometric amounts of AsF_5 yields the salts $Hg_3(AsF_6)_2$ and $Hg_4(ASF_6)_2$. The two salts contain linear discrete mercury polycations Hg_3^{2+} and Hg_4^{2+} respectively. The Hg_3^{2+} cation is also present in the salt $Hg_3.(AlCl_4)_2$.[211] Golden crystals with the composition $Hg_{2.85}.AsF_6$ sparingly soluble in SO_2 are formed in the initial stage of the interaction of mercury with AsF_5. The same compound is a product of the disproportionation of the salt $Hg_4(AsF_6)_2$ on slow cooling of its solution in SO_2:

$$5.44Hg_4(AsF_6)_2 \rightarrow 3.44Hg_3(AsF_6)_2 + 4Hg_{2.86}AsF_6 \downarrow .$$

A compound with a similar cation is also obtained on oxidation of mercury with antimony pentafluoride; it has the composition $Hg_{2.91}SbF_6$. The formal degrees of oxidation of mercury in these salts are 0.35 and 0.34 respectively. A characteristic feature of the crystal structures of the two salts is the presence of infinite intersecting linear chains of mercury atoms arranged in two mutually perpendicular directions (Fig.11). A consequence of this structure is the quasi-one-dimensional behaviour of the salt crystals at the macroscopic level. The bond length in the Hg–Hg chain (2.64×10^{-10} m) is much shorter than in metallic mercury (3.005×10^{-10} m) and is not comparable to the lattice period of the salt. However, the distance between the mercury chains is only 3.085×10^{-10} m, which gives rise to the possibility of an appreciable interaction between the chains.

Thus the systems described possess all conditions for the establishment of the one-dimensional metallic state. The conductivities in the basal planes of the $Hg_{2.86}AsF_6$ and $Hg_{2.91}SbF_6$ crystals σ_{ab} (300 K) are respectively 8.7×10^5 and $\sim 10^5\ \Omega^{-1}\ m^{-1}$. The anisotropy of the conductivity of the $Hg_{2.86}AsF_6$ crystal is $\rho_{ab}/\rho_c \approx 70$ at room temperature. The quantity ρ_{ab} for this salt decreases unusually rapidly on cooling and $\rho_{ab} \approx 10^{-9}\ \Omega$ m already at 4.2 K, which is less than the limit of the measurement. Extrapolution of the $\rho_{ab}(T)$ relation to the absolute zero reveals the absence of a residual resistance. The resistance ρ_c at 4 K decreases abruptly (over a range of 0.2 K) virtually to zero. The disappearance of this transition in magnetic fields directed both parallel to the basal plane and at right angles to it makes it possible to classify it as a superconducting transition. The critical field is minimal if it is directed along the c axis and at $T = 1.4$ K it amounts to 3.8×10^{-2} Wb m^{-2}. In the "normal" state at temperatures less than 30 K and in a field of 10^{-3} Wb m^{-2} the magnetoresistance increases sharply. For $H \neq 0$, a residual resistance appears in the $\rho_{ab}(T)$ relation. The magnetic susceptibility is almost constant in the range 4–300 K; the specific heat C in the range 1.8–5 K is described by the equation $C = \gamma T + \beta T^3$ with an unusually high value of γ.

The study of the elastic and non-elastic reflection of neutrons in the range 10–300 K reveals a phase transition at 120 K corresponding to the ordering of the rigid chains of mercury atoms. At room temperature the salt crystals consist of a network of one-dimensional chains, in the range 300–120 K parallel chains are ordered, and at 120 K order is established between orthogonal systems of chains. At $T < 120$ K the system is three-dimensional.

VIII. CONCLUSION

The study of the quasi-one-dimensional molecular solids examined in this review, which was begun comparatively recently, has developed so effectively that over a short period it has led to the creation of a new scientific field—the chemistry of quasi-one-dimensional metals, including CTC and RIS as well as inorganic, organometallic, and coordination compounds. The number of new objects increases continuously. During the preparation of the manuscript for the press, communications on the synthesis of olefindithiolates with conductivity of their metallic type were published. The conductivity σ_{300} of $Li_{0.75}[Pt(mnt)_2].2H_2O$ crystals is 30–200 Ω^{-1} cm^{-1} and increases slightly up to 250 K.[212] The electrical conductivity of the complex of perylene with

$[Pt(mnt)_2]$, having the composition $(Pe)_2[Pt(mnt)_2]$ increases on cooling, reaching a maximum at 15 K, $\sigma_{300} = 9 \times 10^3\ \Omega^{-1}\,cm^{-1}$,[213] after which it decreases sharply.

The radical-cation salts are being investigated most vigorously at the present time. This was greatly stimulated by the discovery of the superconductivity of the $(TMTSF)_2PF_6$ crystals[214]. As in the series of the isomorphous salts $(TMTTF)_2^+X^-$, where $X^- = BF_4^-$, ClO_4^-, SCN^-, PF_6^-, or Br^- (examined in detail in a review[215]), which undergo the Peierls transition at $T < 100$ K, in the analogous salts $(TMTSF)_2^+X^-$ ($X^- = NO_3^-$, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, or TaF_6^-) the metal–dielectric transition is observed at lower temperatures ($T < 20$ K) or is not observed at all [for example, for $(TMTSF)_2ClO_4$].[216–222] The metallic phase can be stabilised by the application of an appropriate pressure. In the metal–dielectric transition, there is an unusually marked increase of conductivity—up to $10^5\ \Omega^{-1}\,cm^{-1}$.[222]

Studies of nuclear magnetic resonance and magnetism established that the transition to the dielectric phase in $(TMTSF)_2PF_6$ is associated with spin density waves. Consequently we have here a new example of the spin-Peierls instability. The set of numerous experimental facts—the unusual increase of σ, a very high magneto-resistance, and non-linear voltage—current characteristics—suggest the occurrence of one-dimensional superconductivity fluctuations in the salts $(TMTSF)_2X$ at $T < 40$ K.[221] In the salt $(TMTSF)_2 \cdot PF_6$ the transition to a superconducting state has been observed at pressures $p > 9 \times 10^8$ Pa and $T_c = 0.9$ K.[218] This is a superconductor of the second kind with very low critical magnetic fields $H_{C_1}^{\perp} = 3 \times 10^{-3}$ Wb m^{-2} and $H_{C_2}^{\perp} = 3.3 \times 10^{-2}$ Wb m^{-2}.[216] The transition temperature diminishes fairly rapidly with increasing pressure; thus at $p = 2.4 \times 10^9$ Pa it is $T_c = 0.19$ K.[219] The $T_c(p)$ relation is approximately linear: $\partial T_c/\partial p = -8 \pm 1$ K Pa^{-1}. At $p = 6.5 \times 10^8$ Pa the superconducting and dielectric phases coexist, since the metal–dielectric transition temperature at this pressure is 6 K.[223]

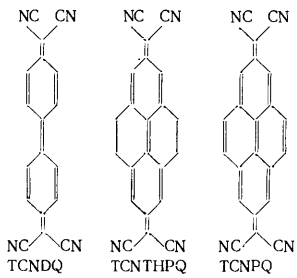
The superconductivity of $(TMTSF)_2AsF_6$ crystals has been observed at $p \geq 1.2 \times 10^9$ Pa and $T_c \leq 1.1$ K.[218] When the pressure is reduced, it is possible to attain $T_c = 1.4$ K at $p = 6.5 \times 10^8$ Pa for the salt $(TMTSF)_2PF_6$ and $p = 10^9$ Pa for the salt $(TMTSF)_2AsF_6$.

The superconductivity of $(TMTSF)_2ClO_4$ ($p = 3 \times 10^8$ Pa), $(TMTSF)_2SbF_6$ ($p = 10^9$ Pa), and $(TMTSF)_2TaF_6$ ($p = 1.1 \times 10^9$ Pa) crystals has been observed[222]. At $p = 10^5$ Pa the superconducting transition in $(TMTSF)_2ClO_4$ is observed at 1.3 K.

Even on the basis of aromatic hydrocarbons, highly conducting radical-cation salts have been obtained and isolated. They have the composition $(Arene)_2^+X^-$, where $X^- = PF_6^-$, AsF_6^-, SbF_6^-, BF_4^-, or ClO_4^- and Arene = naphthalene, fluoranthene, pyrene, perylene, and triphenylene[224]. The salt $(naphthalene)_2^+(PF_6^-)$ exhibits the highest conductivity ($\sigma_{293} = 0.12\ \Omega^{-1}\,cm^{-1}$). Typical conductivities of other salts are in the range 10^{-2}–$10^{-3}\ \Omega^{-1}\,cm^{-1}$.

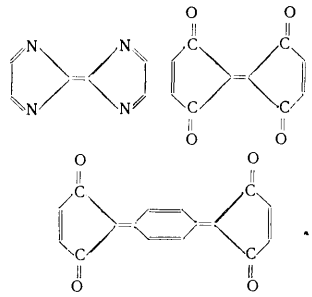
Highly conducting salts of a new donor—tetratellurotetracene (TTeT),—having the composition $(TTeT)_2X$ (X = Cl or Br), were isolated recently[225]. The conductivity σ_{293} of the pelleted specimens is 1–2 $\Omega^{-1}\,cm^{-1}$. The authors were unable to isolate single crystals suitable for the measurement of the electrical conductivity and it is therefore not clear whether the electrophysical properties change significantly following the replacement of sulphur or selenium ions by tellurium.

Publications on the synthesis of new acceptors—tetracyanodiphenoquinodimethane (TCNDQ), tetracyanotetrahydropyrenoquinodimethane (TCNTHPQ), and tetracyanopyrenoquinodimethane (TCNPQ) —have appeared recently[226,227].

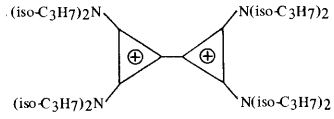


These acceptors form dianions and radical-anions and are apparently stronger acceptors than TCNQ as far as one can judge from their electrochemical potentials. They form CTC with TTF in the form of fine black crystals. However, in our view, acceptors of this kind can hardly be used for the synthesis of compounds with interesting electrophysical properties. It is difficult to select for TCNTHPQ and TCNPQ a donor close to them in linear dimensions, which is one of the conditions for the preparation of CTC of the non-interleaved type[228]. Low solubility is also an obstacle to the preparation of single crystals. Furthermore, in connection with the discovery of the superconductivity of radical-ion salts, the problem of the synthesis of organic superconductors with the highest possible T_c has now become urgent. Apart from the requirements formulated by Krivoshei[228], the components of the CTC or the RIS must satisfy yet another significant condition in order to achieve this[229]: they must exhibit a high polarisability for small linear dimensions.

The synthesis of the acceptors illustrated below is of interest in this sense:



The ways of synthesising such acceptors are being sought nowadays by the authors of the review. The study[230] in which the salt $\{[(iso\text{-}Pr)_2N]_4TF\}^{2+}(ClO_4^-)_2$ (TF = triafulvalene)



was isolated merits attention. The salts of TF and of its substituted derivatives can be used to prepare CTC by exchange reactions (with partial reduction) for the synthesis of RIS.

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Halogen Derivatives of 1,4-Dioxan

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Methods for obtaining mono-, di-, and poly-chlorinated derivatives of 1,4-dioxan by the direct substitution of hydrogen atoms by chlorine are surveyed, together with synthetic reactions yielding fluoro-, chloro-, and bromo-dioxans. Methods of obtaining halogenoalkylated dioxans containing fluorine, chlorine, or iodine atoms are described. Consideration is given to reactions of halogenodioxans making possible their use in organic synthesis, in particular of solvents for polymers. A list of 110 references is included.

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I. INTRODUCTION

1,4-Dioxan (usually termed simply *dioxan*) continually attracts the attention of chemists because it is a specific and perhaps universal solvent meriting the name "organic water". Furthermore, it forms molecular compounds (dioxanates) with many inorganic and organic substances. Such dioxanates are often used in organic synthesis[1]. Dioxan itself and its derivatives also occupy an important position in organic synthesis. The halogen derivatives, in particular chlorodioxans, are especially valuable.

Halogeno-derivatives of dioxan and their reactions have been only partly dealt with in recent monographs and reviews[2-4]. A considerable number of predominantly experimental studies on halogenodioxans and their use in various types of organic syntheses have been reported during past decades.

Direct chlorination of dioxan is the chief method for obtaining chlorodioxans, with replacement of any hydrogen atom forming an α-chlorinated ether. Direct fluorination and iodination of dioxan have not been reported, the corresponding derivatives being obtained by indirect procedures. Iodinated dioxans are completely unknown. Chloro- and bromo-dioxans are extraordinarily reactive: they are used to obtain alkyl- and aryl-dioxans, alkoxy- and aryloxy-dioxans, dihydrodioxin, dioxin, dioxanone, and other compounds based on the dioxan ring.

II. CHLORODIOXANS

Chlorine does not form stable dioxanates, in contrast to bromine and iodine, which at and below room temperature form with dioxan molecular compounds $C_4H_8O_2.X_2$ (X = Br,I). The direct action of chlorine on dioxan involves a vigorous exothermic reaction accompanied by evolution of hydrogen chloride. If the temperature is not controlled, the reaction may terminate in an explosion. The chlorination of dioxan is strongly accelerated by light and by catalysts such as Lewis acids. Chloro-derivatives of various degrees of substitution right up to octachlorodioxan $C_4Cl_8O_2$ can be obtained by the direct chlorination of dioxan. Chlorodioxans having a specified number of chlorine atoms in the ring can be prepared by maintaining a definite régime of chlorination.

Certain difficulties arise in establishing the structure of chlorodioxans. The chlorination of dioxan may lead to the simultaneous formation of many structural isomers and stereoisomers as well as conformers. Furthermore, the reaction is accompanied by chlorolysis with fission of the dioxan ring. Among 45 possible chlorodioxans (counting optical isomers) only 16 are known. The Table gives data on the numbers and properties of possible isomers.

Chlorodioxans*.

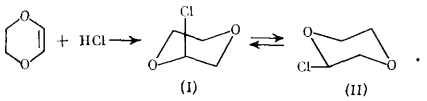
Isomer	N_p	N_k	Properties	Yield, %	Ref.
Mono	1	1	m.p. 62°C/14 mmHg, d_4^{20} 1.276	70	[5]
Di					
2,2	1	1	b.p. 33-35°C/0.5 mmHg, d_4^{20} 1.4797	57	[15]
2,3	2	2	m.p. 53°C (*cis*), 31°C (*trans*)	80—90	[21—23, 25]
2,5	2	1	m.p. 118-120°C	25	[6, 59, 60]
2,6	2	0	—	—	—
Tri					
2,2,3	1	1	m.p. 20, b.p. 60-61°C/1 mmHg	—	[37]
2,2,5	1	0	—	—	—
2,2,6	1	0	—	—	—
2,3,5	4	0	—	—	—
Tetra					
2,2,3,3 (A)	1	1	m.p. 137-140°C	67	[37]
2,2,3,5 (B)	2	1	b.p. 93-95°C/12 mmHg	85	[21, 38, 41]
2,2,3,6 (C)	2	1	m.p. 57-58°C		[21, 38, 41]
2,2,5,5 (D)	1	0	m.p. 59-60°C	33	[21, 38, 41]
2,2,5,6 (E)	2	0	m.p. 70-71°C	—	[62, 67]
2,2,6,6 (F)	1	0	m.p. 100-101°C	25	[37]
2,3,5,6 (G)	5	4	m.p. 143-144°C	10	[21, 38, 60]
Penta					
2,2,3,3,5	1	0	—	—	—
2,2,3,5,5	1	0	—	—	—
2,2,3,6,6	1	0	—	—	—
2,2,3,5,6	4	0	—	—	—
Hexa					
2,2,3,3,5,5	1	2*	m.p. 92 and 94°C	25	[45, 62]
2,2,3,3,5,6	2				
2,2,3,5,5,6	2				
2,2,3,5,6,6	2				
Hepta	2	2	m.p. 56 and 123°C	90	[62, 63]
Octa	1	1	m.p. 108°C	—	[62, 63]

* N_p = number of possible stereoisomers; N_k = number of known isomers; (A)-(G): see Section II, 3b.
** Structure not established.

1. Monochlorodioxan

Monochlorodioxan (2-chloro-1,4-dioxan, dioxanyl chloride) cannot be obtained by the direct action of chlorine on dioxan.

The unstable compound is apparently further chlorinated to dichlorodioxans[5-7]. Monochlorodioxan is usually obtained by the addition of hydrogen chloride to dihydrodioxin in the cold[5]:

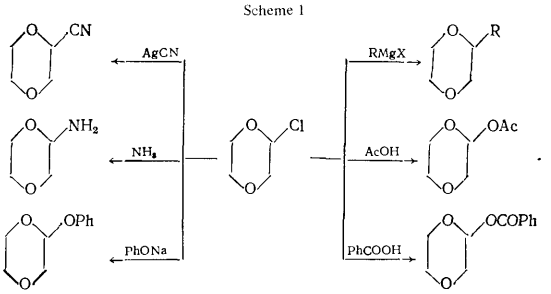


(I) (II)

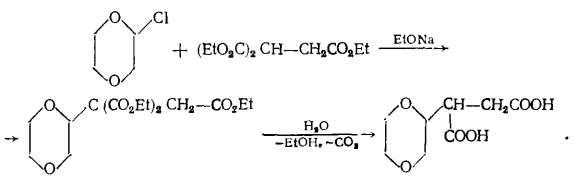
Use of a solvent in this reaction lowers the yield[8]. Nuclear magnetic resonance spectral data have shown[9] that, in virtue of the anomeric effect†, monochlorodioxan exists predominantly in the axial conformation (I), with the position of the conformational equilibrium (I) ⇌ (II) almost unaffected by the polarity of a solvent, (II) being the equatorial isomer.

Monochlorodioxan is unstable and gradually decomposes, especially in the presence of moisture, evolving hydrogen chloride and resinifying. Its instability and great reactivity are explained by the activating influence of ethereal oxygen on the α-chlorine atom. It can be used to obtain other monosubstituted dioxans. Thus heating with silver cyanide yields cyanodioxan, which in turn serves as starting material for the preparation of other monosubstituted derivatives[11]. A series of nucleophilic substitutions of the chlorine atom have been described:

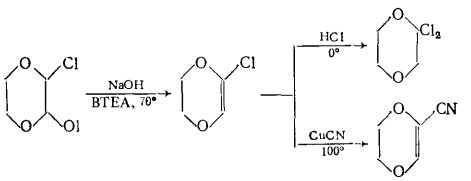
Scheme 1



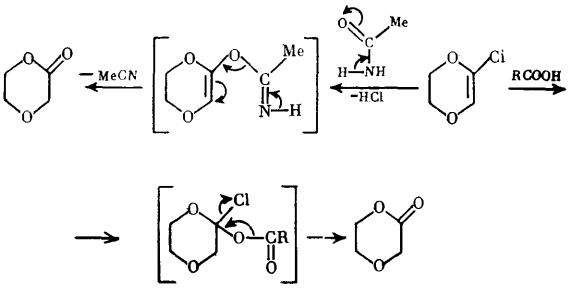
Monochlorodioxan does not form the usual Grignard compounds with magnesium, but it gives 2-alkyldioxans with alkylmagnesium halides RMgX (R = C_2H_5, n-C_4H_9, etc.; X = Cl, Br, I).[8] Amino-, phenoxy-, acetoxy-, and benzoyloxy-dioxans have been obtained in 70–80% yields[12,13]. In the presence of sodium ethoxide monochlorodioxan reacts with triethyl ethane-1,1,2-tricarboxylate to form the 1-dioxanyl triester, which on hydrolysis followed by decarboxylation is converted into dioxanylsuccinic acid[14]:



An important chloro-derivative is 5-chloro-2,3-dihydro-1,4-dioxin, which is usually obtained by the dehydrochlorination of 2,3-dichlorodioxan when heated with dimethylaniline[15] or on pyrolysis[16]. A proposed effective method of dehydrochlorination is the use of 40% caustic soda under the mild conditions of phase-transfer catalysis in the presence of benzyltriethylammonium chloride (BTEA), which gives a 65–68% yield of the chlorodihydro-derivative[17]:

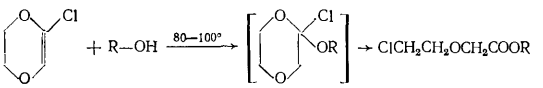


5-Chloro-2,3-dihydrodioxin exhibits the typical properties of a chlorovinyl ether: vigorous addition of hydrogen chloride takes place in the cold in conformity with Markovnikov's rule to give 2,2-dichlorodioxan[15], and it reacts comparatively readily with copper cyanide to form 5-cyanodihydrodioxin[18]. Vigorous reaction takes place also with carboxylic acids to give high yields of dioxan-2-one and the corresponding acid chlorides[16]. This reaction is of practical interest (in the case of acetic acid), since dioxanone has proved a valuable solvent for certain polymers; similar results are obtained with acetamide[19]:



R = Me (84), CH_2Cl (100), Ph (62), *p*-$O_2NC_6H_4$ (38)[2] ‡.

When 5-chloro-2,3-dihydrodioxin is heated with a primary alcohol or a phenol, however, a vigorous reaction leads to fission of the ring and formation of a 2'-chloroethoxyacetic ester, apparently also involving addition at the double bond[16]:



R = Me (54), Et (71), n-Bu (81), Ph (91.5), *p*-MeC_6H_4 (87).

2. Dichlorodioxans

Three of the seven possible structural isomers of dichlorodioxan are known.

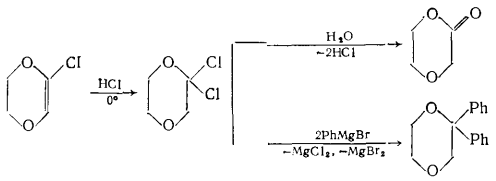
(a) 2,2-Dichlorodioxan

Small quantities of 2,2-dichlorodioxan are detected among the products of the direct chlorination of dioxan, but this reaction is unsuitable for preparative purposes. As already noted, 2,2-dichlorodioxan is obtained in entirely satisfactory yields by the addition of hydrogen chloride to 5-chloro-2,3-dihydrodioxin in the cold[15]. It is not very stable and is

† The anomeric effect is the predominance of the axial conformation of an α-substituent relative to a heteroatom as a consequence of steric or electronic effects, dipole–dipole interaction, the state of hybridisation of the atoms, etc.[10]

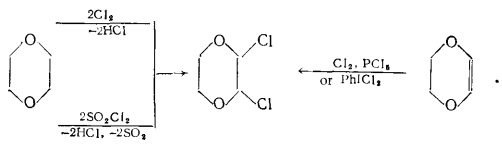
‡ Parentheses enclose percentage yields of dioxanone.

readily hydrolysed to dioxan-2-one, but it reacts normally with phenylmagnesium bromide to give 2,2-diphenyldioxan[15]:



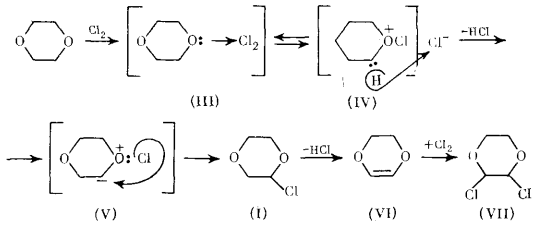
(b) 2,3-Dichlorodioxan

The readily accessible 2,3-dichlorodioxan, which is prepared by the direct chlorination of dioxan, is most important and interesting for the chemistry of the latter, and was first obtained in 1931.[20] It was later shown that chlorination is catalysed by addition of a chloride of copper, iron, manganese, nickel, tin, or iodine[8,21], to give a yield of ~ 90%. The patent literature indicates[22,23] that good yields are obtained by the action of chlorine on dioxan in the vapour phase (120 °C) in the presence of phosphorus(III), phosphorus(V), or antimony(V) chloride as catalyst. Sulphuryl chloride can also be used as chlorinating agent[24], with which an effective procedure has been developed to give an 80% yield[25]; 2,3-dichlorodioxan can be obtained from dihydrodioxin by the addition of chlorine[11,26] and also by the action of phosphorus pentachloride or dichloroiodobenzene[19]:



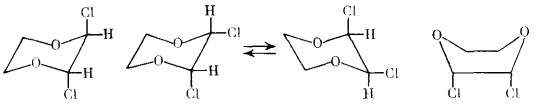
Incidentally, the latter reactions serve as proof of the positions of the chlorine atoms.

The mechanism of the direct chlorination of dioxan to 2,3-dichlorodioxan at 90 °C and at higher temperatures, when polychlorodioxans are obtained, apparently comprises a series of consecutive primary reactions[2,5,6]:



Chlorine acts on dioxan to form an unstable dioxanate (III), which in the presence of Lewis acids is strongly polarised and converted into the ionic dioxanate (IV). The latter eliminates a molecule of hydrogen chloride to form the carbanion (V), which is converted into unstable monochlorodioxan (I). At high temperatures this undergoes dehydrochlorination to dihydrodioxin (VI). Lastly, this product adds a molecule of chlorine to give the final reaction product—stable 2,3-dichlorodioxan (VII).

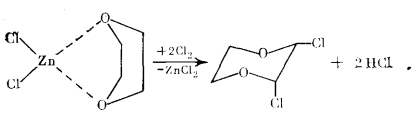
2,3-Dichlorodioxan is known in the form of two isomers (VIII) and (IX), which differ in melting point, infrared spectrum, and dipole moment[15]:



	(VIII) ($Cl_{ax,ax}$)	(IX) ($Cl_{ax,eq}$)	(X) ($Cl_{eq,ax}$)	(XI)
M.p., °C	31	53		
Infrared, cm^{-1}	875	948		
μ, D	0	1.6		

Polarity, polarisability, and n.m.r. spectral data at and below room temperature (down to −42 °C) indicate that both isomers have a chair conformation[27-34]. The more stable *trans*-isomer (VIII) has the diaxial chair conformation ($Cl_{ax,ax}$). The less stable *cis*-isomer (IX) also has a chair conformation, with an axial–equatorial arrangement of the chlorine atoms ($Cl_{ax,eq}$), which undergoes inversion to form an equilibrium mixture with the conformation (X) ($Cl_{eq,ax}$)[31,34]: the statement that it is present as the rigid boat (XI)[29] is incorrect. Chlorination of dioxan in the absence of a solvent gives predominantly the isomer (VIII) with a little (~ 4%) of isomer (IX); in boiling tetrachloromethane a mixture of almost equal quantities of (VIII) and (IX) is obtained, which can be separated by crystallisation. The less stable isomer (IX), when heated with aluminium chloride or sulphuryl chloride, is rapidly and almost quantitatively converted into the *trans*-isomer (VIII)[15].

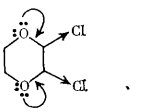
The almost pure isomer (IX) can be prepared by chlorinating dioxan in the presence of zinc chloride[34]. The stereochemistry of the reaction can be attributed to formation of the dioxanate $C_4H_8O_2.ZnCl_2$, in which the dioxan ring is in the boat conformation[35], with the oxygen atoms coordinated with the zinc atom:



Chlorination of such a dioxanate becomes sterically preferred for the formation of *cis*-2,3-dichlorodioxan (IX)[34].

2,3-Dichlorodioxan is toxic: contact with the skin or inhalation of its vapour leads to dizziness, headache, nausea, and inflammation of the mucous membrane of the eye, symptons which may continue for several days. Partial alleviation is provided by the inhalation of ammonia[15].

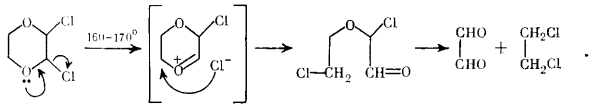
The chemical properties of 2,3-dichlorodioxan are consistent with electronic effects arising from the strong polarisation of the carbon–chlorine bonds and displacement of the *p*-electrons of the ethereal oxygen atoms conjugated with those bonds



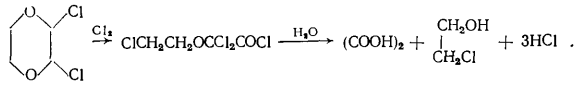
This explains the poor aqueous solubility and the inability to form dioxanates. 2,3-Dichlorodioxan is extremely reactive, mainly in three directions—cleavage of the dioxan ring, nucleophilic replacement of chlorine atoms, and elimination of the elements of hydrogen chloride.

Under the influence of various factors the ring in substituted dioxans is generally opened more readily than is the extremely stable ring of dioxan itself. Thus ring fission

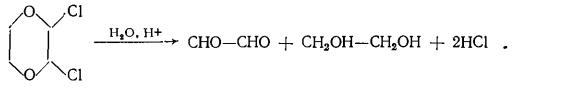
occurs readily when 2,3-dichlorodioxan is heated. Thermal decomposition of this compound is assumed to involve ionisation of one of the chlorine atoms and its migration across the ether link, with intermediate formation of 2,2′-dichloroethoxyacetaldehyde, which then decomposes into glyoxal and 1,2-dichloroethane[36]:



The dioxan ring undergoes cleavage also in the chlorolysis of 2,3-dichlorodioxan to the extremely reactive 2,2,5-trichloro-3-oxavaleryl chloride, which can be hydrolysed to oxalic acid, 2-chloroethanol, and hydrogen chloride[37]:

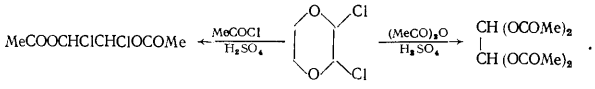


2,3-Dichlorodioxan is comparatively readily hydrolysed when heated with acidified water, being converted into equal quantities of glyoxal and ethylene glycol[20,38]:

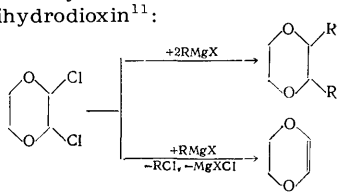


The *cis*-isomer is hydrolysed more rapidly than the *trans*-isomer by a factor of 14.[15] Hydrolysis of this compound has been proposed for the preparation of glyoxal[36,38].

Heating 2,3-dichlorodioxan with excess of acetic anhydride or acetyl chloride mixed with concentrated sulphuric acid also opens the dioxan ring, with the formation respectively of ethanediylidene tetra-acetate (in 70% yield) or 1,2-dichloroethylene diacetate[18]:

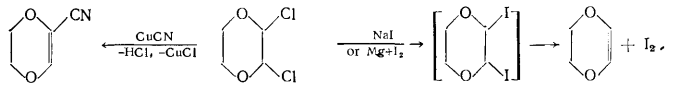


The chlorine atoms in 2,3-dichlorodioxan undergo nucleophilic substitution with rather greater difficulty than do those in the usual α-halogenated ethers. However, several reactions are known in which under certain conditions both chlorine atoms are replaced by various groups to give 2,3-disubstituted dioxans. Thus 37–44% yields of 2,3-dialkyldioxans are obtained by the action of Grignard reagents catalysed by additions of ethereal solutions of anhydrous zinc or cadmium chloride[8,39]. Similarly, arylmagnesium halides yield *trans*-diaryldioxans[26,40–42], substitution in this case being accompanied by elimination of chlorine atoms with the formation of dihydrodioxin[11]:

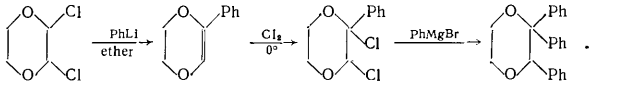


R=Me, Et, n-Pr, n-Bu, CH_2=CH—CH_2, Ph, *p*-ClC_6H_4, *p*-BrC_6H_4; X=Cl, Br .

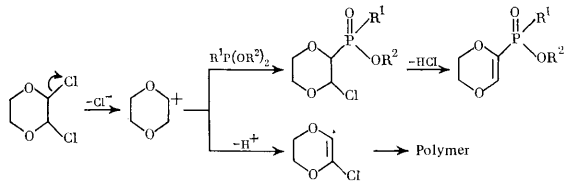
2,3-Dichlorodioxan also undergoes dechlorination when heated with sodium iodide[8] or with a mixture of magnesium and iodine[7], the yield of dihydrodioxin reaching 81% in the latter case. These reactions apparently involve intermediate formation of unstable 2,3-di-iododioxan, which immediately breaks down into dihydrodioxin and molecular iodine. 2,3-Dichlorodioxan reacts quite smoothly with copper cyanide, when 5-cyanodihydrodioxin is formed as a consequence of dehydrochlorination and substitution of the remaining chlorine atom[18]:



Phenyl-lithium reacts similarly to form unstable 2,3-dihydro-5-phenyldioxin (in 31% yield), which on cautious chlorination gives 2,3-dichloro-2-phenyldioxan; the latter can be converted by phenylmagnesium bromide into 2,2,3-triphenyldioxan (yield 54%)[43]:



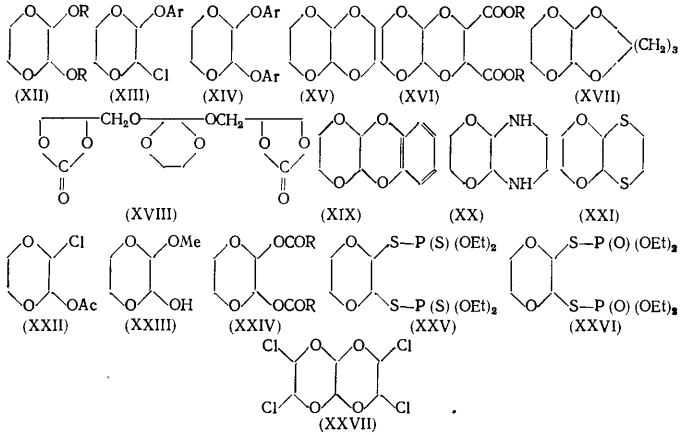
Application of the Michaelis–Becker reaction to 2,3-dichlorodioxan and a sodium dialkyl phosphite yields small quantities (< 20%) of phosphonylated derivatives of dihydrodioxin[44]. The same work showed[44] that the 2,3-dichloro-compound undergoes the Arbuzov reaction with difficulty, and only under comparatively severe conditions does it form with esters of tervalent phosphorus *C*-phosphonylated derivatives of dioxan in relatively low yields (< 40%):



R^1 = Me, Et, *p*-ClC_6H_4, EtO, n-PrO, n-BuO etc.;
R^2 = Et, n-Pr, n-Bu, etc.

The low reactivity of 2,3-dichlorodioxan is most probably due to steric hindrance.

Many nucleophilic substitutions of the chlorine atoms in 2,3-dichlorodioxan have been reported, yielding various 2,3-disubstituted dioxans

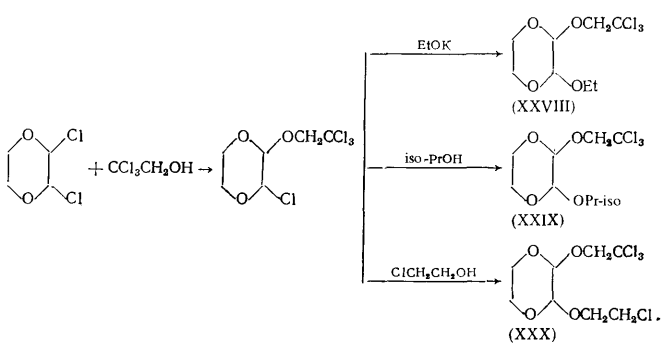


Thus alcoholic sodium ethoxide forms 2,3-diethoxydioxan (XII: R = C_2H_5),[20] but heating with benzyl alcohol gives crystalline 2,3-dibenzyloxydioxan (XII: R = $C_6H_5CH_2$).[45] A monoalkyl ether of ethylene glycol, e.g. 2-ethoxyethanol, forms 2,3-bis-(2-ethoxyethyl)dioxan (XII: R = $C_2H_5OCH_2CH_2$), which has been proposed as a high-boiling solvent for polymers and as a softening agent conferring antistatic properties on films[46]. Under certain conditions the chlorine atoms can

be replaced in stages. Thus heating 2,3-dichlorodioxan with a phenol ArOH (Ar = C_6H_5, o-$CH_3C_6H_4$, p-$CH_3C_6H_4$, 2,4-$Cl_2C_6H_3$) gives 45–52% yields of 2-aryloxy-3-chlorodioxans (XIII)[18,47], in which the second chlorine atom is readily replaced to form 2,3-diaryloxydioxans (XIV) (yields 40–60%)[18]. Heating 2,3-dichlorodioxan with ethylene glycol gives decahydro-1,4,5,8-tetraoxanaphthalene (XV)[18,45,48], the yield of which reaches 77% when the reaction is conducted in pyridine[49]. With the dimethyl or diethyl ester of (+)-tartaric acid 2,3-dichlorodioxan forms the corresponding ester of (−)-decahydro-1,4,5,8-tetraoxanaphthalenedicarboxylic acid (XVI: R = CH_3, C_2H_5), which after saponification and decarboxylation is converted into decahydrotetraoxanaphthalene (XV)[45,50]. Heating 2,3-dichlorodioxan with propane-1,3-diol forms 2,3-trimethylenedioxydioxan (XVII)[51], but 3-hydroxypropylene carbonate gives crystalline dioxan-2,3-bisoxypropylene dicarbonate (XVIII), used for the preparation of water-insoluble resins, which have been suggested as additives for the sizing of yarn and in papermaking[52]. When 2,3-dichlorodioxan is heated with pyrocatechol in xylene, crystalline decahydro-2,3-benzo-1,4,5,8-tetraoxanaphthalene (XIX) is obtained[40,41,45]. Ethylenediamine resembles dihydric alcohols in forming a bicyclic heterocycle, decahydro-1,4-dioxa-5,8-diazanaphthalene (XX)[19], and ethanedithiol forms decahydro-1,4-dioxa-5,8-dithianaphthalene (XXI)[53]. Heating with acetic acid in toluene initially forms 3-chlorodioxanyl acetate (XXII)[54], which with methanolic sodium methoxide gives 3-methoxydioxanol (XXIII)[18]. Diesters (XXIV: R = CH_3, C_2H_5) are obtained when 2,3-dichlorodioxan is heated with potassium acetate in acetic acid or with silver acetate in benzene, and in still higher yields (80–90%) with ammonium carboxylates[18].

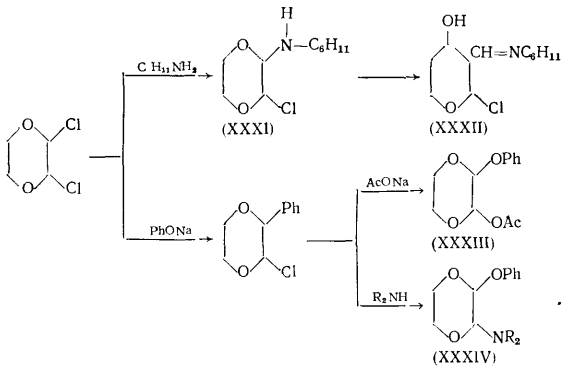
Dioxan rings are present in insecticides having practical value. For example, the diphosphorodithioate (XXV) (Delnav) is obtained by heating 2,3-dichlorodioxan with *OO*-diethyl hydrogen dithiophosphate in the presence of catalytic quantities of zinc chloride or a tertiary amine[55,56]. Delnav exists as *cis*- and *trans*-isomers, the former being considerably more toxic. Another product is Delnav-P-*O* (XXVI), obtained similarly from *OO*-diethyl hydrogen thiophosphate[56]. When *trans*-2,3-dichlorodioxan is dissolved in concentrated sulphuric acid and kept at 40 °C for 24 h, hydrogen chloride is evolved and a compound $C_6H_6Cl_4O_4$ is obtained, to which the structure 2,3,6,7-tetrachlorodecahydro-1,4,5,8-tetraoxanaphthalene (XXVII) was attributed[57].

As already remarked, the chlorine atoms in 2,3-dichlorodioxan can be replaced in stages, with the formation of 3-substituted 2-chlorodioxans, which can be isolated as individual compounds. Such monochlorinated dioxan derivatives undergo further vigorous nucleophilic substitution of the remaining chlorine atom. Thus heating 2,3-dichlorodioxan in benzene with 2,2,2-trichloroethanol gives crystalline 2,2′2′,2′-tetrachloro-3-ethoxydioxan (yield 50%), which on treatment with potassium ethoxide, propan-2-ol, and 2-chloroethanol forms compounds (XXVIII)–(XXX) respectively[58]:



(XXVIII) (XXIX) (XXX)

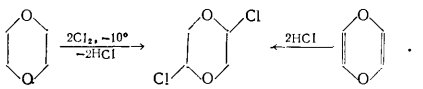
In the absence of atmospheric moisture 2,3-dichlorodioxan undergoes an exothermic reaction with cyclohexylamine, forming 2-chloro-3-*N*-cyclohexylaminodioxan (XXXI), which when heated undergoes fission of the dioxan ring and conversion into the azomethine (XXXII)[19]:



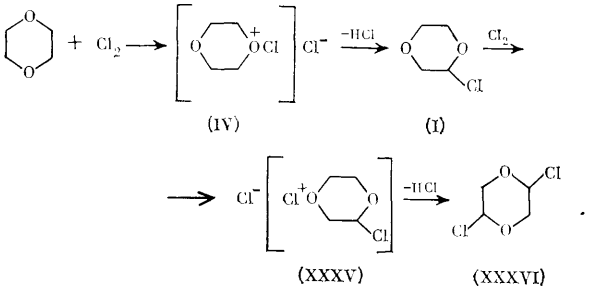
2-Chloro-3-phenoxydioxan, obtained from 2,3-dichlorodioxan and sodium phenoxide, gives 3-phenoxydioxanyl acetate (XXXIII) when heated with sodium acetate, and forms 2-amino-3-phenoxydioxans (XXXIV) with secondary amines[18].

(c) 2,5-Dichlorodioxan

2,5-Dichlorodioxan is obtained by chlorinating dioxan in the cold (between −47 and −5°), when ~ 25% of the crystalline *trans*-isomer is isolated from the complicated mixture that results[6,59]; this product is obtained also by the addition of hydrogen chloride to dioxin[60];



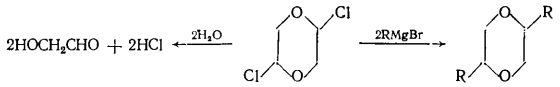
Chlorination of dioxan at low temperatures[2,5,6] also gives initially the chlorodioxanate (IV) and monochlorodioxan (I). In contrast to chlorination at high temperatures, e.g. 90 °C, elimination of hydrogen chloride from chlorodioxan (I) is greatly retarded. As a consequence, a second chlorine molecule is able to form the unstable dioxanate (XXXV) with the second ethereal oxygen atom in chlorodioxan, and 2,5-dichlorodioxan (XXXVI) results from (XXXV) by known reactions:



(IV) (I) (XXXV) (XXXVI)

2,5-Dichlorodioxan is a typical α-chloro-ether, but as a consequence of its molecular symmetry is more stable than the 2,3-dichloro-isomer. Nevertheless, it is gradually hydrolysed by moisture, evolving hydrogen chloride, and when boiled with water the dioxan ring opens to give an almost quantitative yield of glycollaldehyde, which is proof of the structure of 2,5-dichlorodioxan[60]; with alkyl- and

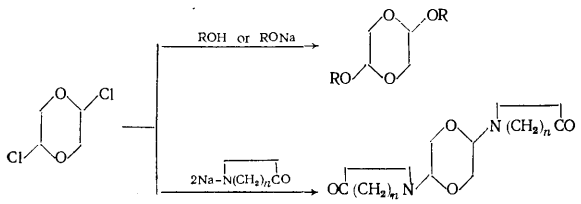
aryl-magnesium bromides mixtures of *cis*- and *trans*-2,5-disubstituted dioxans are formed[6,61]:



R=Me, n-Bu, Ph, *p*-MeC_6H_4 .

In the reaction with phenylmagnesium bromide the yield of 2,5-diphenyldioxan reaches 95%.[6]

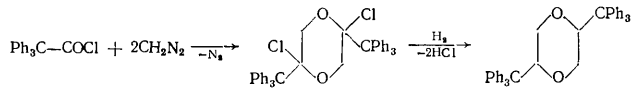
Dioxan derivatives containing substituents at positions 2 and 5 are obtained by the action of nucleophilic reagents on 2,5-dichlorodioxan[62–64]:



n=3–5

R=$CH_2CH{=}CH_2$, CH_2CH_2Cl, $CH_2CH_2CH_2Cl$, CH_2CH_2Br, CH_2CH_2CN, CH(CN)Me, Ph, 2,4-$Cl_2C_6H_3$, $PhOCH_2CH_2$, 4-$ClC_6H_4OCH_2CH_2$, 1-$C_{10}H_7$.

It was reported[65] that reaction between triphenylacetyl chloride and diazomethane gives crystalline 2,5-dichloro-2,5-bistriphenylmethyldioxan (m.p. 133 °C), which on reduction is converted into 2,5-bistriphenylmethyldioxan:



3. Polychlorodioxans

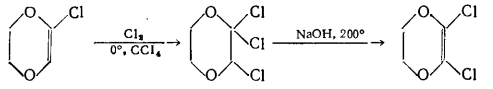
Tri-, tetra-, hexa-, hepta-, and octa-chlorodioxans have been obtained by the direct chlorination of dioxan and also indirectly, and their properties have been described. No report has yet appeared of the existence of pentachlorodioxan.

The results of the direct action of chlorine on dioxan exhibit a peculiar temperature dependence[2]: after the predominant formation of 2,5-dichlorodioxan at subzero temperatures[6,59], another one or two hydrogen atoms are replaced with every additional 10-deg rise in temperature, so that tetrachlorodioxans are formed at +10 °C, but hexachlorodioxans at +20 °C. To obtain heptachlorodioxan the temperature must be raised to 30–40 °C. The yields of polychlorodioxans obtained by low-temperature chlorination are usually small. Further action of chlorine at temperatures above 40 °C leads to gradual chlorolysis with degradation of the ring. When 80 °C is reached, a violent exothermic reaction suddenly begins, with swelling, charring, and even ignition of the reaction mixture. In this case the instability of the various chlorination products makes it very difficult to isolate individual compounds. Under reaction conditions under which this peculiar temperature barrier in the region of 80–90 °C has been surmounted, and especially in the presence of a catalyst such as iodine, tin(II) chloride, etc., the chlorination of dioxan again proceeds comparatively smoothly with, as already noted, the formation predominantly of 2,3-dichlorodioxan. At 110–170 °C highly chlorinated polychlorodioxans are obtained. The high-temperature chlorination of dioxan also yields complicated mixtures, including not only chlorodioxans but also chlorolysis products; its mechanism has remained almost uninvestigated, but is assumed to involve radical reactions.

The stability of polychlorodioxans towards hydrolysis and other chemical actions increases with the number of chlorine atoms in the ring. Thus tetrachlorodioxans (other than the 2,2,3,3-isomer) and more highly chlorinated dioxans can be steam-distilled without appreciable decomposition[62]. Polychlorodioxans exert an insecticidal action similar to that of DDT.[19]

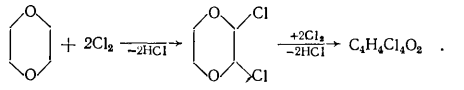
(a) 2,2,3-Trichlorodioxan

2,2,3-Trichlorodioxan has not been obtained by the direct chlorination of dioxan: it can be prepared by the addition of chlorine to 5-chloro-2,3-dihydrodioxin[37]. Thermal alkaline dehydrochlorination converts 2,2,3-trichlorodioxan into 5,6-dichloro-2,3-dihydrodioxin (yield 52%):



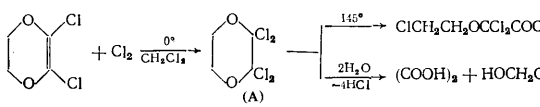
(b) Tetrachlorodioxans

Seven of the possible isomeric chlorodioxans are known (Table, A–G), formed in small quantities in the preparation of 2,3-dichlorodioxan by the chlorination of dioxan at 90 °C.[60] The yields increase with rise in the temperature of the reaction (to 135–140 °C) and increase in its duration[38,41]. It is assumed that the production of tetrachlorodioxans is preceded by the formation of 2,3-dichlorodioxan[21,38,41,45,62]:



The chlorination of 2,3-dichlorodioxan at 135 °C does indeed give an 85% yield of a mixture of isomers, from which individual tetrachlorodioxans have been isolated[37,41,62]. Some have been prepared by other methods.

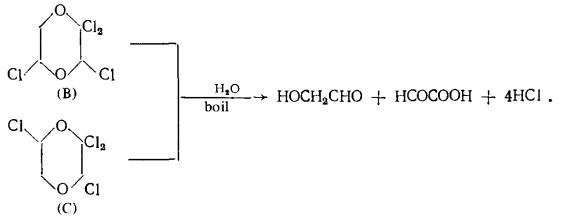
The report[66] that 2,2,3,3-tetrachlorodioxan (A) could be obtained by chlorinating 2,3-dichlorodioxan at 155–160 °C proved incorrect. As shown later, only chlorolysis products of dioxan are obtained, but (A) can be prepared in quite good yield by the addition of chlorine to 5,6-dichloro-2,3-dihydrodioxin[37]. The tetrachloro-isomer (A) is a quite stable compound, decomposing only when heated above the melting point, to form 2,2,2'-trichloroethoxyacetyl chloride, but on prolonged boiling with water it is hydrolysed and converted into oxalic acid, ethylene glycol, and hydrogen chloride:



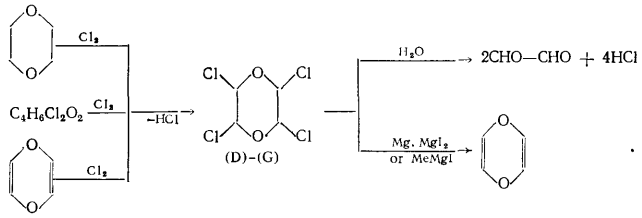
(A)

The structures of tetrachlorodioxans (B) and (C), isolated in small quantities from the products of the chlorination of 2,3-dichlorodioxan, have not been accurately established: the liquid isomer (B) is assumed to be 2,2,3,5-tetrachlorodioxan, and the crystalline isomer (C) 2,2,3,6-tetrachlorodioxan. Both compounds also resist the action of water, being hydrolysed only after prolonged boiling with water (for

5–6 h), which converts them quantitatively into glycollaldehyde, glyoxylic acid, and hydrogen chloride[21,38,41]:



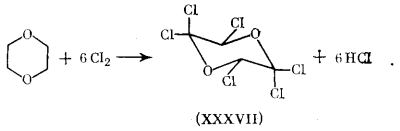
The symmetrical 2,3,5,6-tetrachlorodioxans are especially interesting, with five possible stereoisomers depending on the disposal of the chlorine atoms. The four crystalline stereoisomers that have been prepared and characterised (D)–(G) differ in melting point. Tetrachlorodioxans (D)–(F) are obtained by the chlorination respectively of dioxan[21,38], 2,3-dichlorodioxan[21,41], and 2,5-dichlorodioxan[62,67]; the isomer (G) results from the addition of chlorine to 1,4-dioxin[21,38,60]:



Compounds (D)–(G) are also stable towards water, and can be distilled in steam without appreciable hydrolysis[60], but on being boiled with water for 2–3 h decompose quantitatively into glyoxal and hydrogen chloride[38]. When heated with magnesium, magnesium iodide, or methylmagnesium iodide they are dehydrochlorinated to 1,4-dioxin. Both reactions provide evidence of the positions of the chlorine atoms in these tetrachlorodioxans[60].

(c) Hexachlorodioxans

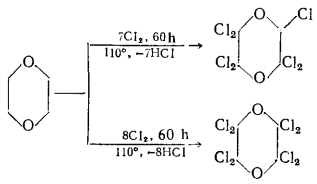
When chlorine is passed into dioxan at 110 °C for a long time (~ 50 h), two isomeric hexachlorodioxans differing in melting point can be isolated from the reaction mixture in a total yield of 25%.[45,62] The one melting at 94 °C and having zero dipole moment was regarded[48] as 2,2,3,5,5,6-hexachlorodioxan (XXXVII):



(XXXVII)

(d) Hepta- and octa-chlorodioxans

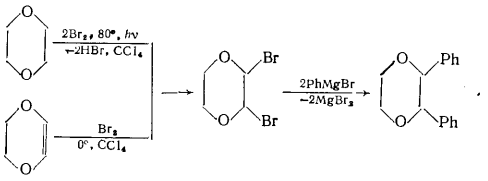
Still more prolonged chlorination of dioxan (at 110 °C for ~ 60 h) gives a good yield of two stereoisomeric heptachlorodioxans, which differ considerably in melting point. Introduction of the eighth chlorine atom into the dioxan ring takes place slowly and with difficulty. The octachlorodioxan isolated from the reaction mixture crystallises well[62,63]:



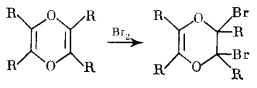
Heptachlorodioxan is so stable that it begins to evolve hydrogen chloride only when heated with concentrated sulphuric acid to 150 °C, without darkening of the reaction mixture. It does not split off hydrogen chloride when heated with aqueous alkalis or with aqueous–alcoholic silver nitrate solution, and a mixture of concentrated sulphuric acid and potassium permanganate has hardly any effect[62]. Heptachlorodioxan possesses well developed insecticidal properties, surpassing the γ-isomer of DDT in its action on individual species of ants[2].

III. BROMO- AND FLUORO-DIOXANS

Bromodioxans have been far less studied than have chlorodioxans. In the cold dioxan forms with bromine a dioxanate $C_4H_8O_2.Br_2$[1,68–70], which when heated decomposes with opening of the dioxan ring and formation of bromoethane, hydrogen bromide, etc.[38,71]. On ultraviolet exposure in tetrachloromethane dioxan is smoothly brominated[72] to crystalline 2,3-dibromodioxan (yield 75%, m.p. 71.5–73.5 °C); this dibromide is obtained also in good yield (92%) by the addition of bromine to dihydrodioxin in tetrachloromethane in the cold[5,26]:



Similarly, 2,3-dihydro-5-phenyldioxin adds bromine to give 2,3-dibromo-5-phenyldioxin[43]. It is interesting that under the same conditions 1,4-dioxin[60] and 2,3,5,6-tetraphenyl-1,4-dioxin[73] add only one bromine molecule to form substituted dihydrodioxins:

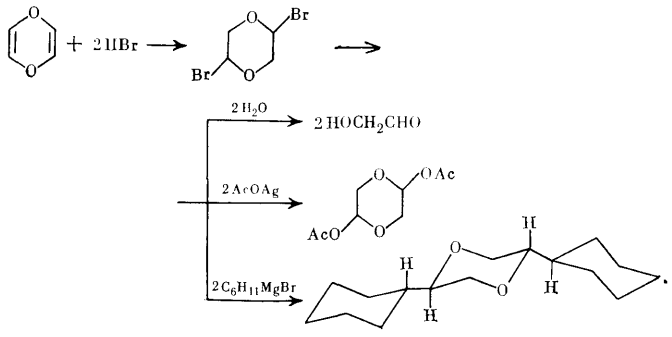


R = H, Ph .

2,3-Dibromodioxan is unstable, and is gradually decomposed by atmospheric moisture, with the evolution of hydrogen bromide. Its structure has been proved by its reaction with phenylmagnesium bromide, when 2,3-diphenyldioxan is obtained[5].

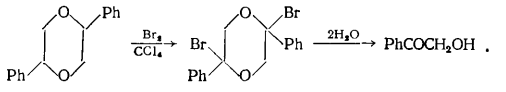
2,5-Dibromodioxan has been obtained in good yield (90%) by passing anhydrous hydrogen bromide into a cold chloroform solution of 1,4-dioxin. It is thermally unstable, darkening at 104 °C, and decomposing at 134 °C. Its structure has been confirmed by hydrolysis: brief boiling with water readily gives a quantitative yield of glycollaldehyde. When 2,5-dibromodioxan is heated with silver acetate in toluene,

both bromine atoms are replaced by acetoxy-groups to form dioxan-2,5-ylene diacetate[74]:

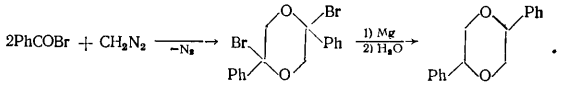


With cyclohexylmagnesium bromide 2,5-dibromodioxan forms (in 20% yield) 2,5-dicyclohexyldioxan as the *trans*-diequatorial conformer (according to n.m.r. spectral data)[75].

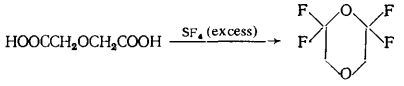
2,5-Diphenyldioxan is readily brominated to 2,5-dibromo-2,5-diphenyldioxan, which on hydrolysis is converted into hydroxymethyl phenyl ketone[6]:



As with the chloro-derivative, the action of diazomethane on benzoyl bromide gives 2,5-dibromo-2,5-diphenyldioxan, which is converted by the successive action of magnesium and water into 2,5-diphenyldioxan (yield 62%)[65]:



The action of sulphur tetrafluoride on a diglycollic ester forms the extremely stable liquid 2,2,6,6-tetrafluorodioxan[76,77]:

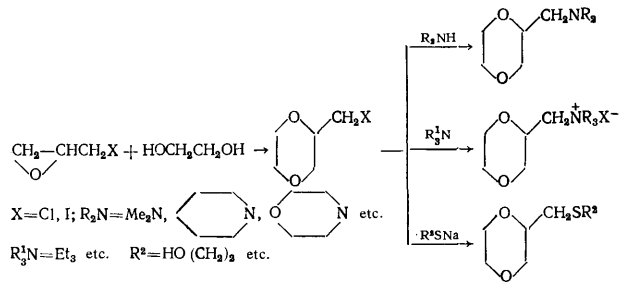


IV. HALOGENOALKYLDIOXANS

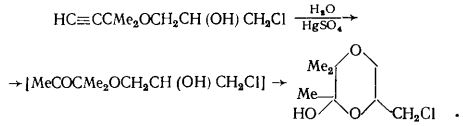
A considerable number of dioxans halogenated in side-chains are known. The halogen atoms usually undergo ready nucleophilic substitution with preservation of the dioxan ring. The best known and most thoroughly studied are the chloro- and iodo-derivatives.

1. Halogenoalkyldioxans

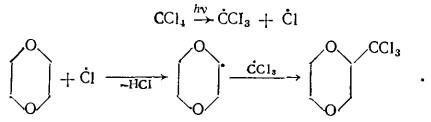
Condensing epoxypropyl chloride and iodide respectively with ethylene glycol in the presence of concentrated sulphuric acid yields 2-chloromethyl- and 2-iodomethyl-dioxans[78], which react readily with secondary and tertiary amines and also with thiols to give alkylated dioxans containing nitrogen or sulphur atoms in the alkyl groups[79,80]:



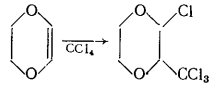
Under the conditions of the Kucherov reaction 1-chloro-5,5-dimethyl-4-oxahept-6-yn-2-ol undergoes hydration and cyclisation to 6-chloromethyl-2,3,3-trimethyldioxan-2-ol[81]:



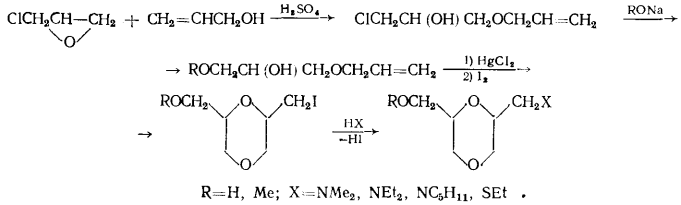
Prolonged (~ 100 h) ultraviolet exposure of a solution of tetrachloromethane in dioxan results in radical reactions, the products of which include crystalline trichloromethyldioxan (m.p. 136–138 °C) together with hydrogen chloride, chloroform, and hexachloroethane[78]:



An analogous mechanism is involved in the addition of tetrachloromethane to dihydrodioxin in the presence of azoisobutyronitrile to form 2-chloro-3-trichloromethyldioxan[82]:

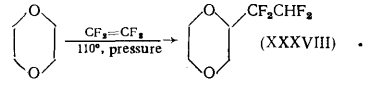


Several 6-substituted iodomethyldioxans have been obtained from epoxypropyl chloride and allyl alcohol, in which the iodine atom is readily exchanged by the action of nucleophiles, as expected, usually forming mixtures of *cis*- and *trans*-2,6-disubstituted dioxans[83–85]:

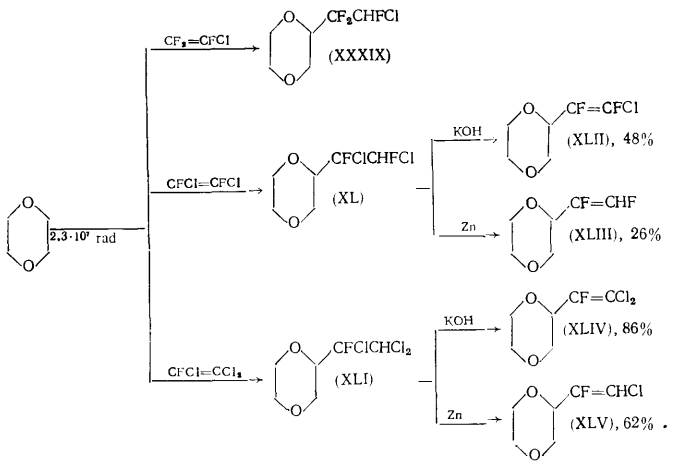


R=H, Me; X=NMe_2, NEt_2, NC_5H_{11}, SEt .

Some interest attaches to fluoroalkyldioxans, obtained from dioxan and organofluorine compounds by free-radical reactions initiated by exposure to ultraviolet radiation or γ-rays, as well as in the presence of peroxy-compounds. According to a patent[86] dioxan reacts with tetrafluoroethylene when heated in the presence of benzoyl peroxide under pressure, with the formation of 1′,1′,2′,2′-tetrafluoroethyldioxan (XXXVIII):

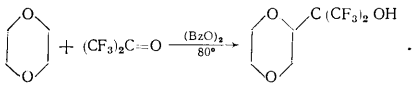


Dioxan reacts with equimolecular proportions of chlorofluoroalkenes on exposure to γ-rays to form liquid chlorofluoroethyldioxans (XXXIX)–(XLI) in yields of ~ 55%[87]:



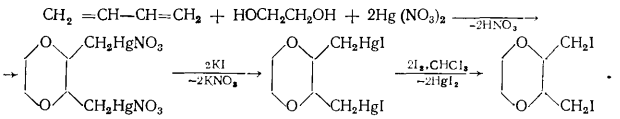
Treatment of the products (XL) and (XLI) with potassium hydroxide or zinc dust converts them into the chlorofluorovinyldioxans (XLII)–(XLV)[88].

Dioxan condenses with hexafluoroacetone on ultraviolet irradiation or on heating with benzoyl peroxide to form crystalline dioxanylbistrifluoromethylmethanol (yield 25%)[89]:



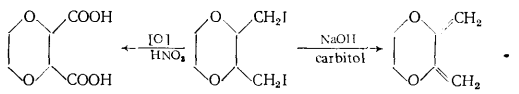
2. Bishalogenoalkyldioxans

Application of Nesmeyanov and Lutsenko's method[92] to buta-1,3-diene and ethylene glycol gave by a series of consecutive reactions 2,3-bisiodomethyldioxan (yield 56%) as a mixture of *cis*- and *trans*-isomers (m.p. 77 and 90 °C) with the latter predominating[90,91]:



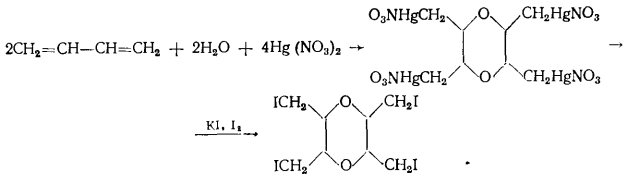
If the reaction is conducted in a strongly acid medium, e.g. in nitric acid, the quantity of the *trans*-isomer is greatly increased.

This *trans*-isomer served as starting material for obtaining a series of 2,3-disubstituted dioxans. Thus oxidation of the di-iodide with nitric acid gives dioxan-*trans*-2,3-dicarboxylic acid (m.p. 175 °C), and heating with alkali in an inert solvent forms a readily polymerisable conjugated diene:

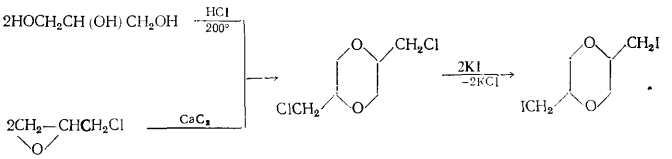


The latter product, 2,3-dimethylenedioxan, forms a crystalline adduct with maleic anhydride (m.p. 82 °C).

If the reaction between butadiene and aqueous mercury(II) nitrate is conducted in the absence of ethylene glycol, and the product is then treated successively with potassium iodide and iodine, 2,3,5,6-tetrakisiodomethyldioxan is obtained, apparently with intermediate formation of 2,3,5,6-tetrakisnitratomercurimethyldioxan[91]:

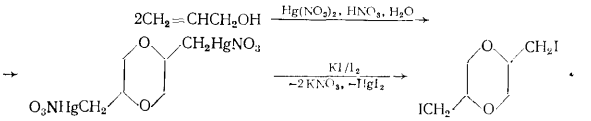


Early papers[93–95] described 2,5-bishalogenomethyldioxans under the names "diepichlorhydrin" and "diepi-iodohydrin". The former was obtained by heating glycerol with hydrochloric acid, and the latter from the former by heating with alcoholic potassium iodide:

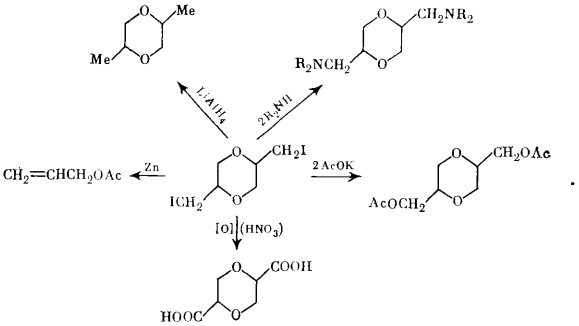


The structure of these compounds was later reliably established as *trans*-2,5-bishalogenomethyldioxans[90,97,98]. According to a patent[99] a 90% yield of *trans*-2,5-bischloromethyldioxan can be obtained by heating epoxypropyl chloride with calcium carbide in the presence of hexacarbonylbistributylphosphinecobalt as catalyst. The resulting dichloride reacts with alcoholic potassium iodide to form crystalline *trans*-2,5-bisiodomethyldioxan (m.p. 158 °C).

The bisiodomethyl derivative can be synthesised also by condensing two molecules of allyl alcohol in the presence of mercury(II) nitrate in aqueous nitric acid and then treating the products with iodine and potassium iodide[90,93,95,96]. In these stereospecific reactions *trans*-2,5-bisnitratomercurimethyldioxan is obtained initially in almost quantitative yield, and with potassium iodide and iodine gives a 90% yield of the di-iodide:

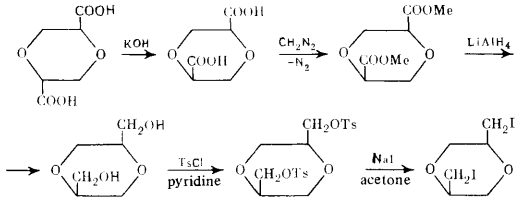


2,5-Bisiodomethyldioxan is of interest in view of the many S_N reactions involving the two reactive iodomethyl groups and yielding *trans*-2,5-dimethyldioxans in which the methyl groups are substituted. Thus heating with concentrated ammonia forms 2,5-bisaminomethyldioxan[93,97], and with morpholine and 2,6-dimethylmorpholine the 2,5-dimorpholino- and 2,5-bis-2′,6′-dimethylmorpholino-dioxans respectively[100]. Brief heating of the di-iodide with potassium acetate in acetic acid involves initial replacement of one iodine atom by an acetate group, but on longer heating two iodine atoms are substituted to give dioxan-2,5-ylenedimethyl diacetate[97]:

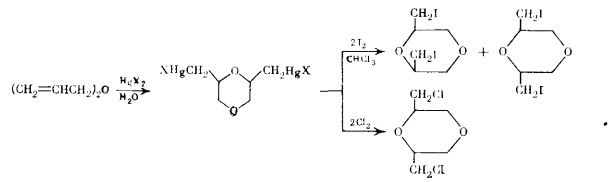


An attempt to reduce the di-iodide with zinc in acetic acid or in alcohol opens the dioxan ring and forms allyl acetate or alcohol respectively, but lithium tetrahydroaluminate in ether reduces it to 2,5-dimethyldioxan[101].

Heating the *trans*-di-iodide with concentrated nitric acid oxidises it to dioxan-*trans*-2,5-dicarboxylic acid[90,98], which when heated with potassium hydroxide isomerises into the *cis*-dicarboxylic acid. This last product can be converted by a series of consecutive reactions into *cis*-2,5-bisiodomethyldioxan (m.p. 97 °C)[97]:

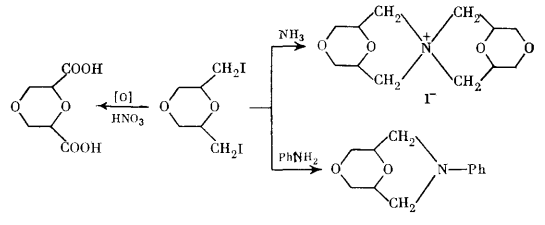


Diallyl ether condenses extremely readily with mercury(II) acetate or chloride in aqueous solution to give an 85% yield of 2,6-bischloromercurimethyldioxan, which on treatment with iodine or chlorine is smoothly converted into respectively 2,6-bisiodomethyl- or 2,6-bischloromethyl-dioxan[92]:



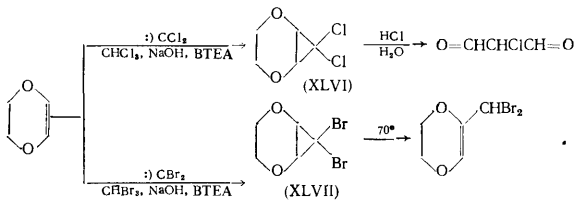
It was established by chemical methods that 2,6-bisiodomethyldioxan is a mixture of *cis*- and *trans*-isomers[98,102]. It is interesting that the former has the higher melting point (90 and 70 °C). The relative stability of the *cis*-isomer is attributed to its greater molecular symmetry, the possibility of its existing as a conformation with a diequatorial arrangement of the iodomethyl groups. In the *trans*-isomer one iodomethyl group occupies an axial position[98].

Here the known facts concerning the greater stability of *cis*- than of *trans*-1,3-disubstituted cyclohexanes can be appropriately compared in terms of the equatorial–polar concept[103]. For steric reasons the former isomer, unlike the latter, forms morpholine derivatives on reaction with ammonia or aniline[98,102]; both isomers are oxidised by hot nitric acid, being converted into the corresponding isomeric dioxan-2,6-dicarboxylic acids without change in the geometric configuration[98]:



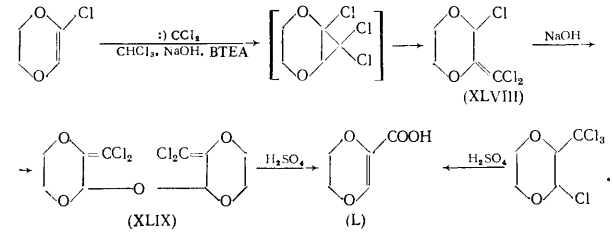
3. Reactions of Halogenocarbenes with Dioxins and Dihydrodioxins

Halogenocarbenes react readily with dioxin and with dihydrodioxin. The adduct of the latter with dichlorocarbene was described first in 1974[104] and then in subsequent papers[105,106]. Detailed investigation showed[107] that, with dichlorocarbene generated from chloroform by the action of 50% caustic soda under conditions of phase-transfer catalysis in the presence of benzyltriethylammonium chloride, dihydrodioxin gives a very good yield (> 90%) of 7,7-dichloro-2,5-dioxabicyclo[4,1,0]heptane (XLVI), which is relatively unstable and is converted into chloromalonaldehyde when boiled with dilute hydrochloric acid[105]:

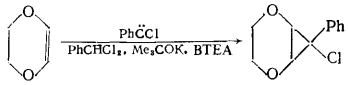


Under analogous conditions dibromocarbene generated from bromoform yields the thermally unstable 7,7-dibromo-2,5-dioxabicyclo[4,1,0]heptane (XLVII), which on moderate heating is converted (with cleavage of the cyclopropane ring) into 5-dibromomethyldihydrodioxin[107].

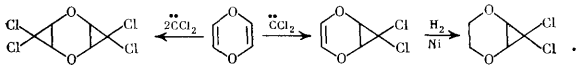
With 5-chlorodihydrodioxin dichlorocarbene does not give a stable adduct at the double bond under conditions of phase-transfer catalysis[108,109]. The bicyclic adduct formed in the course of the reaction is apparently converted into 2-chloro-3-dichloromethylenedioxan (XLVIII), which in an alkaline medium gives the bisdichloromethylenedioxanyl ether (XLIX) (yield 37%), from which dihydrodioxin-5-carboxylic acid (L) is obtained (yield 60%)[108], as also by heating 1-chloro-2-trichloromethyldioxan with sulphuric acid:



The reaction of dihydrodioxin with chlorophenylcarbene generated from benzylidene dichloride and potassium t-butoxide gives 7-chloro-7-phenyl-2,5-dioxabicyclo[4,1,0]heptane[106,110]:



1,4-Dioxin also reacts vigorously with dichlorocarbene generated from methyl trichloroacetate by the action of sodium methoxide[106]. Addition takes place at either one or two double bonds depending on the proportions of the reactants. In the former case 7,7-dichloro-2,5-dioxabicyclo-[4,1,0]heptene is obtained (yield 56%), which on hydrogenation is reduced to the known adduct of dihydrodioxin with dichlorocarbene; in the latter case a double adduct is formed—4,4,8,8-tetrachloro-2,6-dioxatricyclo[5,1,0]octane (yield 34%):



---oOo---

In conclusion it can be stated that halogenodioxans form a group of compounds of interest to organic chemists that has been by no means completely investigated. Individual representatives have a well defined physiological effect and possess insecticidal properties. Among dioxan derivatives the most valuable are those containing chlorine atoms in the ring. Further development of methods of preparation and study of their reactions will undoubtedly give valuable new information for the theory and practice of organic synthesis.

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Reactions of Pyrylium Salts with Nitrogen-containing Nucleophiles

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New data on reactions of pyrylium salts with nitrogen-containing nucleophiles, occurring both with retention of the pyrylium ring and with recyclisation, are considered. The extensive possibilities for the employment of pyrylium salts in the synthesis of many functional compounds of the aliphatic and aromatic series and of different nitrogen- and oxygen-containing three-, five-, six-, and seven-membered heterocycles, including condensed heterocycles, are demonstrated.
The bibliography includes 184 references.

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I. INTRODUCTION

The vigorous development of the chemistry of pyrylium salts observed in recent years is associated not only with the enormous theoretical interest in the reactions of the carboxonium cation but also with the possibility of using such salts for the synthesis of many aliphatic, aromatic, and heterocyclic compounds, which sometimes cannot be obtained by other procedures. In this sense, the cyclisation reactions of pyrylium salts under the influence of nitrogen-containing nucleophiles are of particular interest. They lead to compounds among which effective biologically active substances, dyes, metal corrosion inhibitors, emulsifying agents, etc. have been found[1,2].

Pyrylium salts, which have a positive charge in the heterocycle, are exceptionally reactive to nucleophiles. The presence of a sextet of π electrons is responsible for the aromatic properties of the pyrylium cation. However, the electronegative oxygen heteroatom promotes a non-uniform electron density distribution in the ring. A high positive charge is therefore concentrated at the 2-, 4-, and 6-carbon atoms, whilst the charge at C(3) and C(5) atoms is quite insignificant, or these atoms are even negatively charged[3,4].

The first stage in the reaction of pyrylium salts with nucleophiles is the addition of the nucleophiles to C(2) or more rarely to C(4). The attack on the 2-position in the pyrylium ring is accompanied by ring opening and recyclisation (the S_NANRORC mechanism). The structure of the reaction product depends on the nature of the nucleophile, the substituents in the pyrylium ring, and the process conditions.

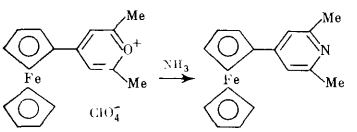
The reactions of pyrylium salts with ammonia, ammonium carbonate and acetate, and certain amines have been partly considered in other reviews[5-8] covering the literature up to 1972. The review of Plas and Streef[9], which deals with the recyclisation of various heterocycles, also presents several examples of the above reactions.

In the present review an attempt has been made to survey the extensive experimental data on the reactions of pyrylium salts with a wide variety of nitrogen-containing nucleophiles, which have accumulated in recent years (up to 1980 inclusive). Some attention has also been devoted to studies published up to 1972 but not included in the reviews quoted above.

Apart from the reactions of monocyclic pyrylium structures, the behaviour of the benzo- and heterocyclic analogues has also been considered, which we believe makes it possible to assess more fully the problem of the reactivity of heteroaromatic cations with *N*-nucleophiles in general.

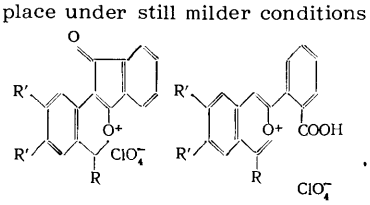
II. INTERACTION OF PYRYLIUM SALTS WITH AMMONIA AND THE SIMPLEST AMINES

In recent years the interaction of pyrylium salts with ammonia led to the synthesis of new compounds of the pyridine series otherwise difficult to obtain[10-23], for example:

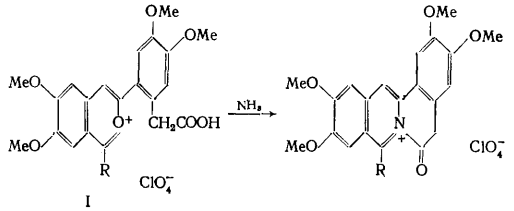


2-Benzopyrylium as well as pyrylium salts condensed with N-, O-, S-, and Se-containing heterocycles react with ammonia to give respectively isoquinoline bases of pyridines condensed with heterocycles. Hitherto unknown isoquinolines or isoquinolines difficult to obtain[24,25], pyridines with condensed cycloalkene rings[26-32] and steroids[33], disteroidopyridines[34], indolo[2,3-*c*]pyridines[35], benzofuro[3,2-*c*]pyridines[36,37], thionaphtheno[2,3-*c*]pyridine[38], selenopheno[3,2-*c*]pyridines[39,40], selenopheno[2,3-*c*]pyridines[41,42], and pyrido[2,3-*d*]pyrimidines[43] have been obtained by this method.

1-Alkyl(aryl)-3,4-diaryl-2-benzopyrylium salts are converted by ammonia into isoquinolines more readily[44] than the 1-alkyl(aryl)-3-aryl-substituted derivatives[45]. The exchange of the ring oxygen atom for nitrogen in 3-aryl-substituted 2-benzopyrylium salts without a substituent in the 1-position[46] and in salts with the electron-accepting carbonyl group[30] takes place under still milder conditions:

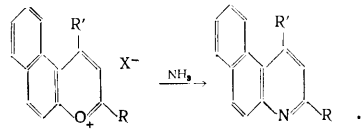


When the salts (I) interact with ammonia, the replacement of the oxygen hetero-atom by nitrogen is accompanied by the formation of a new ring[47]:



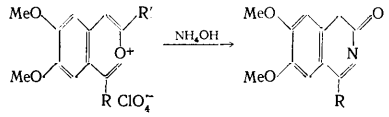
I

1-Benzopyrylium and xanthylium salts cannot be converted into quinolines and acridines by treatment with ammonia[48], but naphtho[*b*]pyrylium salts have been converted into benzoquinoline derivatives in satisfactory yield by reaction with ammonia[49]:



The reactions of 5,6,7,8-tetrahydrochromylium and symmetrical octahydroxanthylium salts with ammonia, leading to 5,6,7,8-tetrahydroquinolines and octahydroacridines, take place under mild conditions[27].

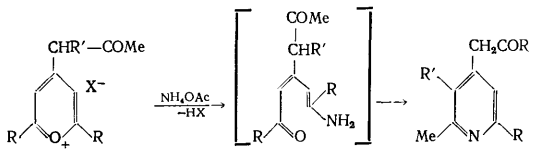
The reaction of 2-benzopyrylium salts containing the 3-OCH_3 group with aqueous ammonia results in the hydrolysis of the intermediate ether and subsequent cyclisation to 3-oxo-4*H*-isoquinoline[50]:



R=Alk, R′=OMe, $PhCOCH_2O$, EtCOO, R″CONH .

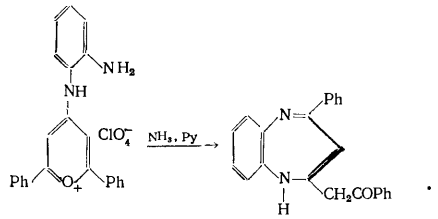
Isoquinolones are formed in high yields also in the reactions of 1-alkyl-3-phenacyloxy-[51] and 1-alkyl-3-acylamino-2-benzopyrylium salts[52] with ammonia. Similarly 1-alkyl-3-methoxy-5,6,7,8-tetrahydro-2-benzopyrylium salts are converted by reaction with ammonia into 1-alkyl-5,6,7,8-tetrahydroquinolones[53]. Pyrylium salts with a free 4-position react with ammonia to form 2,6-disubstituted pyridines[54]. 2-Ethoxyvinylpyrylium salts recyclise to pyridines on reaction with ammonia[55] and the ethoxyvinyl group is simultaneously hydrolysed to the β-hydroxyvinyl group.

The conversion of 4-acetonylpyrylium salt into pyridine with participation of the keto-group of the substituent in the intramolecular cyclisation of the intermediate enamine is of interest[56]:

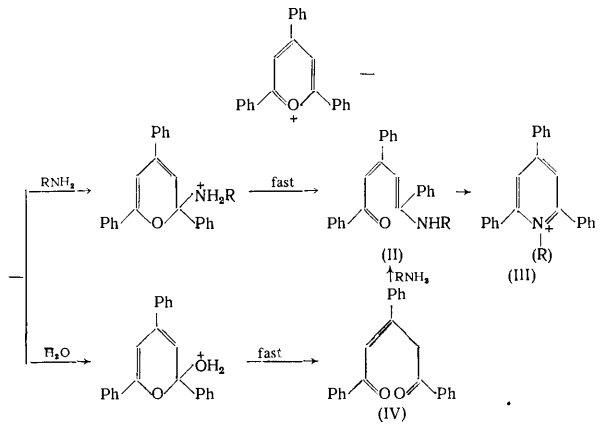


The presence of the electron-donating amino-group in 4-*p*-aminophenylpyrylium salts diminishes somewhat the electrophilicity of the pyrylium ring, but the reaction of these salts with ammonia take place more readily and leads to pyridines[57]. The reaction of *N*-substituted aminopyrylium salts with ammonia proceeds under more severe conditions[19,58]. As a consequence of a still greater delocalisation of the positive charge in the vinylogues of aminopyrylium salts, the ring oxygen heteroatom is not substituted by nitrogen[55].

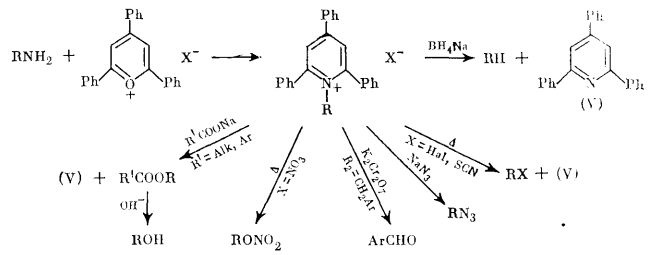
4-(*o*-Aminoanilino)-2,6-diphenylpyrylium perchlorate remains unchanged on being refluxed with ammonium acetate in acetic acid, but the reaction of the salt with ammonia in pyridine leads to its conversion into substituted 1*H*-benzo-1,5-diazepine[59]:



The reactions of arylpyrylium salts with aliphatic amines proceed under mild conditions and with high yields of *N*-alkylpyridinium salts[60,61]. Recent kinetic studies on this reaction by ^{13}C NMR and ultraviolet spectroscopy showed that the rate-limiting stage is the closure of the pyridine ring (II) → (III), which can be catalysed by acids[60,62]:

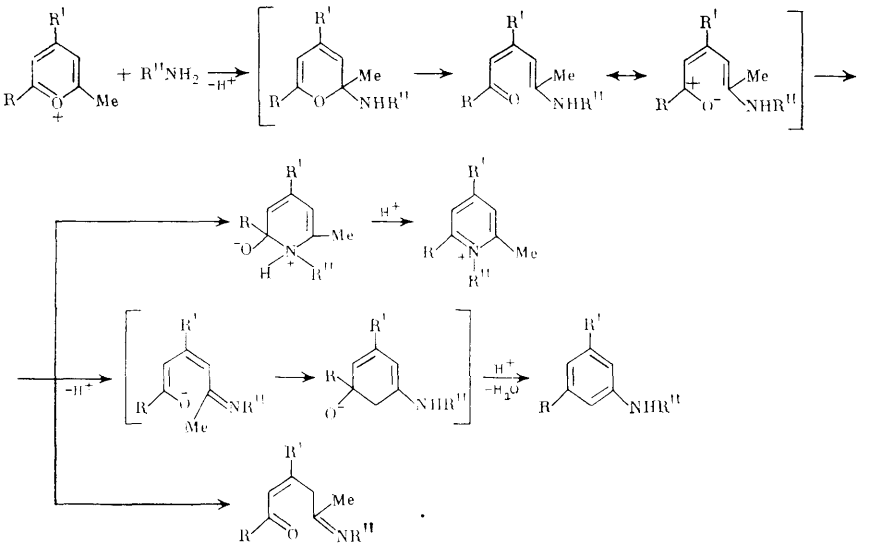


It has also been shown that, together with the main reaction, the diketone (IV) is formed under the influence of traces of water. The diketone (IV) reacts with the amine, giving rise to the pyridinium salt (III), possibly via the aminoketone (II)[60,62]:



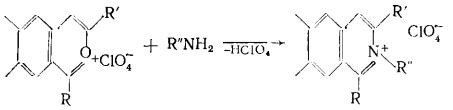
The salts (III) readily split off 2,4,6-triphenylpyridine on being subjected to mild pyrolysis or on treatment with nucleophiles, which makes it possible to employ the reaction of primary amines with pyrylium salts as an intermediate stage in the conversion of amines into hydrocarbons, ethers, alcohols, alkyl halides, thiocyanates, aldehydes, azides, and other derivatives[60].

Substituted xylidines may be formed in the reaction of 2-methylpyrylium salts with aliphatic amines together with the conversion into pyridinium salts[63]:

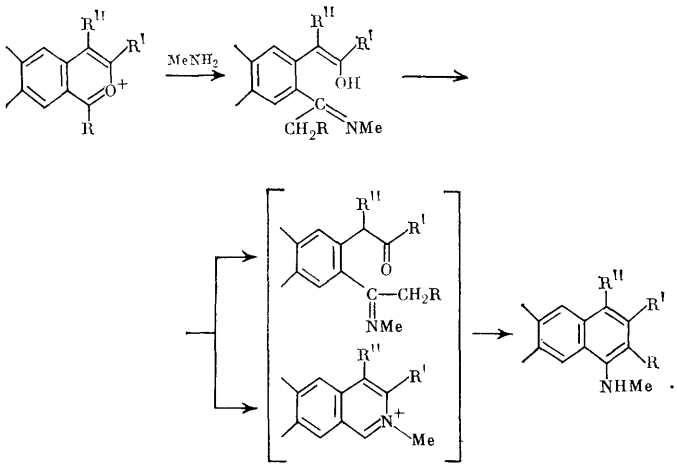


The ratio of the amounts of pyridinium salts and xylidines depends on the nature of the amine. In the case of aliphatic amines and benzylamines the predominant product is pyridinium salts. Cyclohexylamine reacts with 2,4,6-trimethylpyrylium salts to form xylidine, while amines with C_2–C_5 aliphatic groups form xylidines in yields of 30–40%. The interaction with t-butylamine stops at the stage involving the formation of *N*-butylketodienamine, which is the third possible reaction pathway[63].

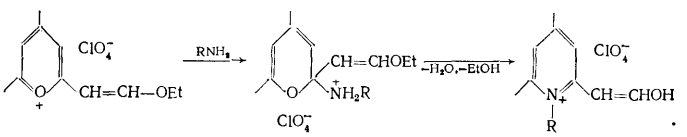
The reaction of 2-benzopyrylium salts with primary amines results in the formation of isoquinolinium salts. Nucleophilic attack by the amine is directed to the most electron-deficient C(1) atom with formation of benzo-1*H*-pyran, which recyclises via an enamine to an isoquinolinium salt[64,65]:



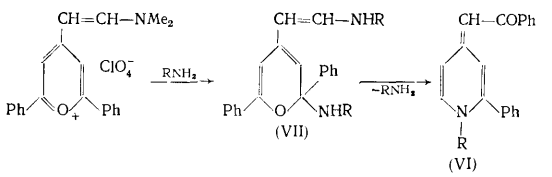
1-Alkyl-3-aryl-substituted 2-benzopyrylium salts, which form α-naphthylamines in the presence of an excess of methylamine, constitute an exception[66,67]. In this case either the second possible version of the cyclisation of the intermediate enamine takes place or the isoquinolinium salt formed recyclises under the influence of the excess amine via the Kost–Sagitullin mechanism[68]:



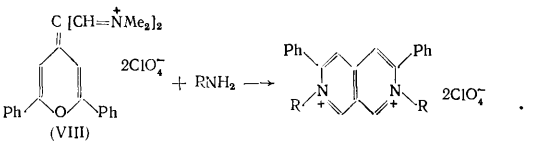
4-Methoxy-2,6-dimethylpyrylium salt reacts with methylamine to form a 4-methoxy- or 4-methylamino-pyridinium salt, depending on the reactant ratio[69]. 2-Benzopyrylium salts with the 3-methoxy-group react with an alcoholic solution of methylamine to form quaternary *N*-methylisoquinolinium salts[50]. Ethoxyvinylpyrylium salts react with aliphatic amines via the mechanism[55]



4-Dimethylaminovinyl-2,6-diphenylpyrylium perchlorate interacts with primary aliphatic amines to form pyridines (VI), which is a result of the recyclisation of the intermediate aminovinylpyran (VII)[70]:

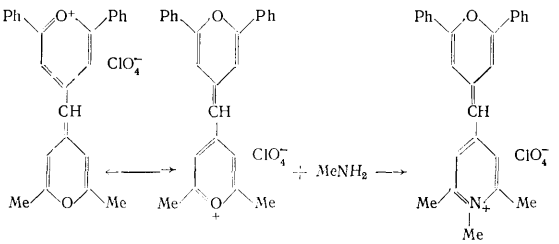


The bisiminium salt (VIII) leads to diquaternised copyrines in an analogous reaction[70]:

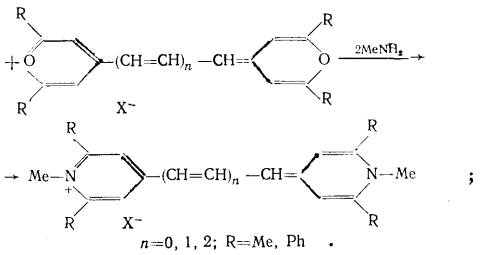


The positive charge in pyrylocyanines is delocalised over the entire mesomeric cation, which diminishes their electrophilicity. Nevertheless, even in alcohol the reaction with

ethylamine leads to pyridopyrylocyanine and in the asymmetric cyanine (IX) the oxygen in the dimethylpyrylium ring is the first to be substituted[71]:



The substitution of the second oxygen atom by nitrogen does not occur in methanol[72,73]. In an aprotic solvent—dimethylformamide (DMF)—it is possible to obtain symmetrical tetramethyl(phenyl)pyrido-derivatives of mono-, tri-, and penta-methinecyanines[71]:

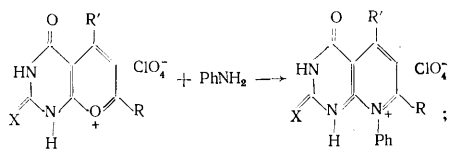


n=0, 1, 2; R=Me, Ph .

Isopropylcyanines exchange only the oxygen heteroatom for the methylamino-group in DMF, while t-butylcyanine does not react with methylamine at all[74].

The conversion of pyrylium and 2-benzopyrylium salts under the influence of aromatic amines into the corresponding *N*-arylpyridinium and isoquinolinium salts has been thoroughly investigated[64,65]. Analogously to their reaction with ammonia, chromylium and xanthylium salts are not converted into quinolinium and acridinium derivatives on reaction with anilines. Nucleophilic attack on the xanthylium salt is directed to the 9-position, which results in the formation of aminoarylxanthenes[48].

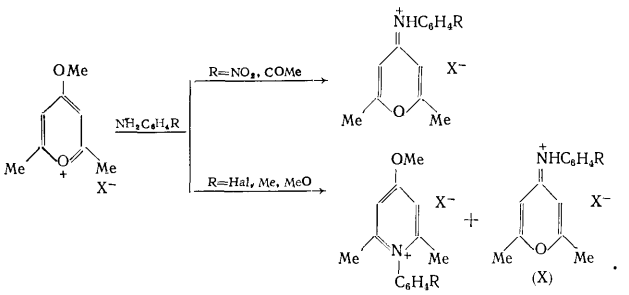
Naphtho[1,2-*c*]- and naphtho[2,1-*c*]-pyrylium salts were made to react with *p*-aminophenol, which yielded benzoquinolinium salts[49]. In contrast to 1-benzopyrylium salts, the condensed pyrylia[2,3-*d*]pyrimidine systems react with aniline to form *N*-phenylpyridinium salts[43]:



X=O, S .

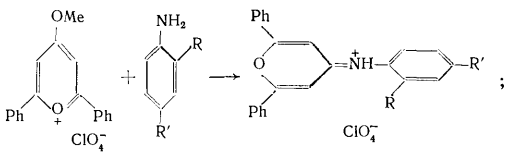
5,6,7,8-Tetrahydrochromylium and symmetrical octahydroxanthylium salts give rise to 5,6,7,8-tetrahydroquinolinium and symmetrical octahydroacridinium salts on treatment with primary amines[75,76].

The reaction of 4-methoxy-2,6-dimethylpyrylium salts with an equimolar amount of *p*-substituted anilines results in the formation of an iminopyran salt (X) together with the 4-methoxypyridinium salt[77]:



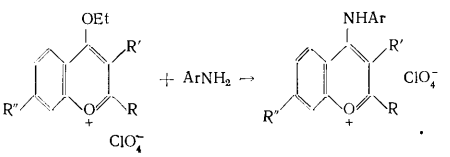
Anilines with electron-accepting substituents form only the products resulting from the attack on the 4-position of the pyrylium ring, i.e. an iminium salt (X). More basic amines with electron-donating substituents attack preferentially the 2-position of the pyrylium cation forming a greater amount of the alkoxypyridinium salt the more pronounced the electron-donating effect of the substituent[77].

It is noteworthy that 4-methoxy-2,6-diphenylpyrylium perchlorate is converted exclusively into pyran iminium salts in the reaction with anilines[59]:

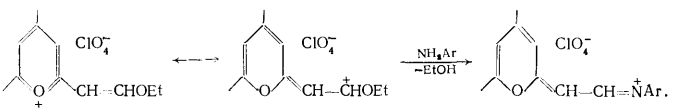


R=H, NH_2, OMe, R′=H; R=H, R′=NH_2, NMe_2, NHCOMe .

The reaction of 4-ethoxychromylium salts with primary amines proceeds analogously[78,79]:



Ethoxyvinylpyrylium salts react with aromatic amines, retaining the pyran ring[55]:

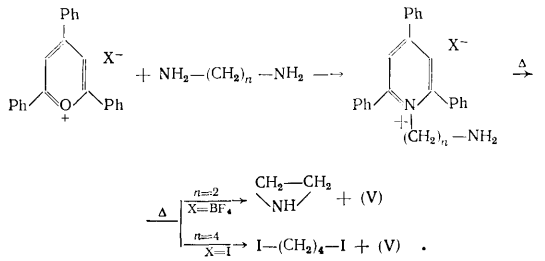


p-Aminophenylpyrylium salts react with aniline only on refluxing in DMF[57].

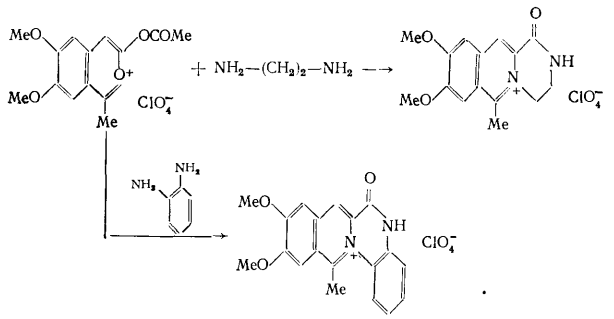
The reactions of pyrylium and 2-benzopyrylium salts with aliphatic and aromatic diamines in molar proportions of 2:1 give rise to bispyridinium salts[65,80-82]. The interaction of pyrylium perchlorate with an equimolar amount of an arylenediamine results in the formation of *N*-aminoarylpyridinium salts[83,84], which react with pyrylium perchlorates to form *m*- or *p*-arylenebispyridinium salts[84] and it is possible to obtain by this procedure compounds with pyridine rings substituted in different ways. *o*-Phenylenediamine reacts with pyrylium salts only via one amino-group, probably owing to steric hindrance. *N*-(*o*-Aminoaryl)pyridinium salts do not form bispyridinium derivatives probably for the same reason[84].

The reactions of equimolar amounts of 2,4,6-triphenylpyrylium salts and aliphatic diamines lead to *N*-aminoalkyl-2,4,6-triphenylpyridinium salts, which have been suggested

for the preparative synthesis of aziridine[85] and di-iodobutane[86] via their pyrolytic decomposition:

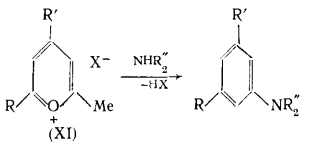


It is of interest that 2-benzopyrylium salts with the 3-methoxycarbonyl group react with certain diamines via two reaction centres[87]:



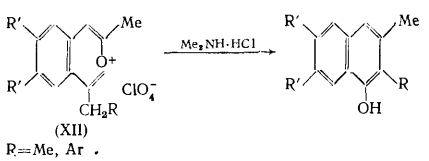
The same pyrylium salts react with *p*-phenylenediamine or 1,8-diaminonaphthalene and are converted into *N*-aminoaryl-substituted quaternary isoquinolinium salts[87].

Pyrylium salts having a 2-methyl or methylene group [compounds (XI)] react with secondary amines and are converted under mild conditions into *N*-substituted anilines[88-90]:



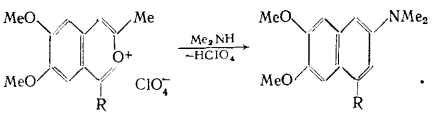
The basicity of the amine plays a significant role in this process. Thus the reaction with highly basic dialkylamines takes place vigorously without heating[88,89]. The reaction of the less basic indoline with the salt (XI, X = ClO_4^-, R = R′ = 4-$MeOC_6H_4$) does not result in the formation of the corresponding *N*-arylindoline[89].

1-Methyl-2-benzopyrylium salts react with cyclic and aliphatic secondary amines to form dialkylaminonaphthalenes[65]. An anomalous reaction of 1-ethyl(benzyl)-substituted 2-benzopyrylium salts (XII) with dimethylamine in ethanol, resulting in the formation of α-naphthols, was discovered recently[91]:



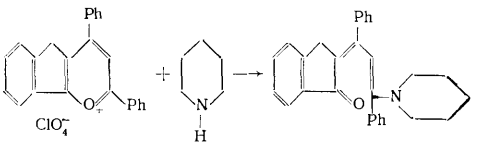
The same reaction takes place when the perchlorate (XII) is acted upon by alkali[92], i.e. the dimethylammonium salt has a catalytic effect on the recyclisation of the 2-benzopyrylium cation with participation of the water present in the alcohol.

The perchlorates (XII, R = H or Me) react with gaseous dimethylamine and recyclise to tertiary β-naphthylamines, which can be accounted for only by the initial attack of the nucleophile on the C(3) position[93]:

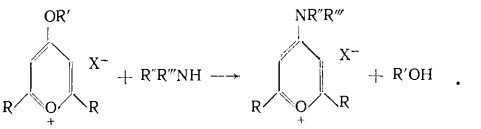


Thieno- and seleno-[2,3-c]pyrylium salts react analogously with dimethylamine[94].

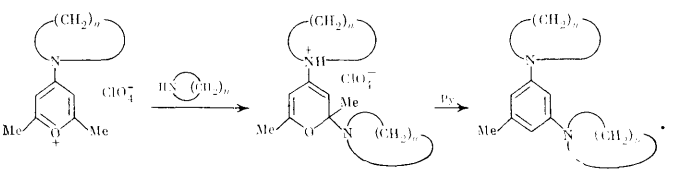
Arylpyrylium salts without an alkyl group in the 2-position are quantitatively converted into dialkylaminoketones on treatment with two equivalents of a secondary aliphatic amine[32,62], for example:



2- or 4-Alkoxypyrylium salts react with secondary aliphatic and heterocyclic amines, retaining the pyrylium ring[58,69,88,95,96]:

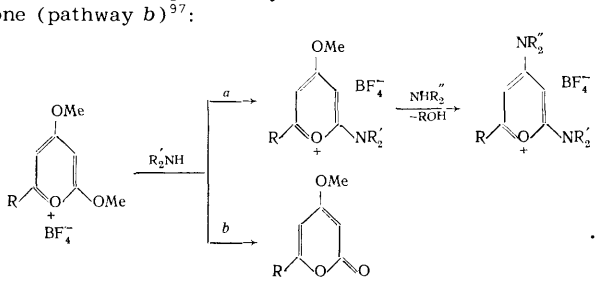


An excess of the amine as well as an increase of temperature promote the formation of the product of the addition of two moles of the secondary amine, which, on heating in pyridine, recyclises to an *m*-diaminobenzene derivative[58]:



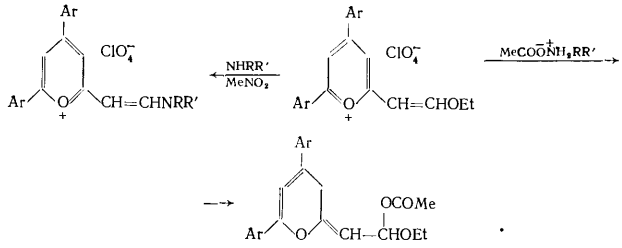
2-Phenylpyrylium salts do not form similar bisadducts.

The reactions of 2,4-dimethoxypyrylium salts with secondary amines proceeds via two pathways: the main pathway involves nucleophilic substitution of the C(2) atom (pathway *a*), while the minor pathway involves the methylation of the amine, i.e. the attack on and dissociation of the O–CH_3 bond with formation of a quaternary ammonium salt and an α-pyrone (pathway *b*)[97]:

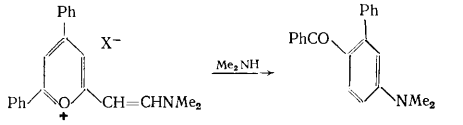


The reaction of an excess of a secondary amine results in the conversion of a 2-amino-4-ethoxypyrylium salt into a 2,4-diaminopyrylium salt[98].

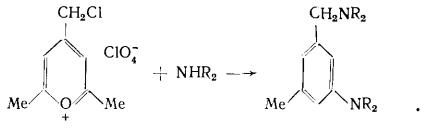
2-Ethoxyvinylpyrylium salts react with secondary amines to form either aminovinylpyrylium salts or acetal-acylals, depending on the solvent employed[55]:



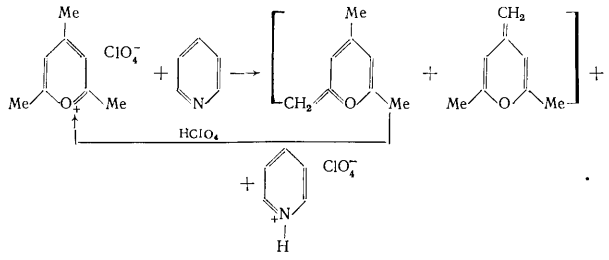
The reaction of aminovinylpyrylium salts with secondary amines can involve the substitution of one amino-group by the other[70]. 2-Dimethylaminovinyl-4,6-diphenylpyrylium is converted into a benzoylaniline on reaction with dimethylamine[99]:



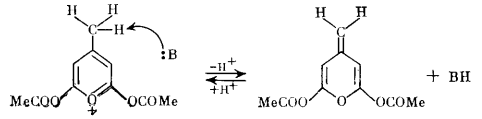
The halogen in 4-halogeno-2,6-diphenylpyrylium salts is readily substituted on reaction with secondary cyclic and alicyclic amines, various 4-dialkylaminopyrylium perchlorates being formed[100]. 4-Chloromethyl-2,6-dimethylpyrylium perchlorate reacts with secondary amines both in the 2-position of the pyrylium ring and via the substituent in the methyl group, forming aromatic diamines[101]:



The reaction of 2,4,6-trimethylpyrylium perchlorate (TMPP) with triethylamine, pyridine, benzimidazoles, imidazoles, quinoline, and pyrazoles takes place with deprotonation of the methyl group of the pyrylium cation[102-104]:



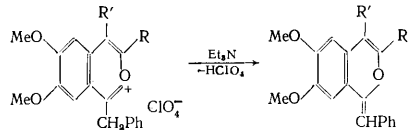
The study of the infrared spectra of the pyridinium perchlorates formed in the reaction with selectively 2- or 4-deuterated TMPP showed that the proton is split off from both the 2-CH_3 and 4-CH_3 groups[102]. The resulting methylenepyrans, which are extremely reactive, undergo further transformation into methylenepyran hexamers, whose structure could not be determined[103]. Comparatively stable methylenepyrans can be obtained only in the presence of effective electron-accepting substituents in the pyran ring. Thus a methylenepyran has been isolated and spectroscopically characterised in the reaction of a 2,6-dimethoxycarbonyl-4-methylpyrylium salt with pyridine[105]:



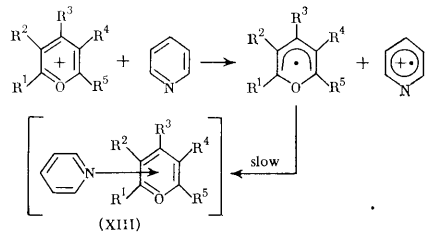
It is of interest that aniline acts on this salt similarly to pyridine.

The dimerisation of 4-methylflavylium perchlorate in pyridine is also believed[106,107] to proceed via the intermediate formation of methylenepyran.

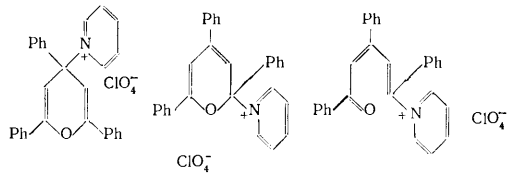
On treatment with triethylamine in an anhydrous medium, 1-benzyl-2-benzopyrylium salts give rise to stable benzylideneisochromenes[108]:



On dissolution in anhydrous pyridine, polyarylpyrylium salts generate pyranyl radicals[109], the EPR spectra of which are identical with those of the radicals formed on reduction of the corresponding pyrylium salts with zinc[110,111]:

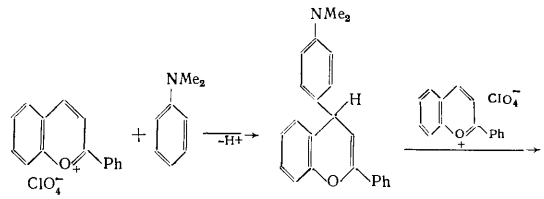


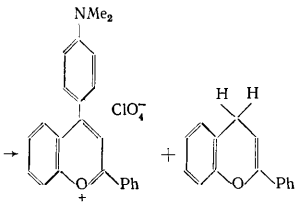
The pyranyl radicals react slowly with pyridine to form donor–acceptor complexes (XIII). It has been established that a small amount of products of the addition of pyridine to the 4- or 2-position of the pyrylium ring and an acyclic valence isomer of the latter are present in the pyridine solution of 2,4,6-triphenylpyrylium perchlorate (TPPP) in addition to the complex (XIII, $R^1 = R^3 = R^5 = Ph$; $R^2 = R^4 = H$)[112]:



It has been shown that TPPP forms charge-transfer complexes also with triphenylamine and its derivatives[113].

Pyrylium and 1-benzopyrylium salts with a free 2- or 4-position react with aryl-substituted tertiary amines and heterocyclic compounds having an excess of electrons to form aminoaryl or heteroaryl-pyrylium salts[15,114-116], for example compound (XIV):

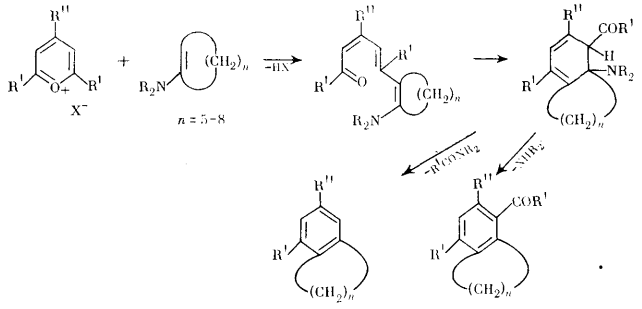




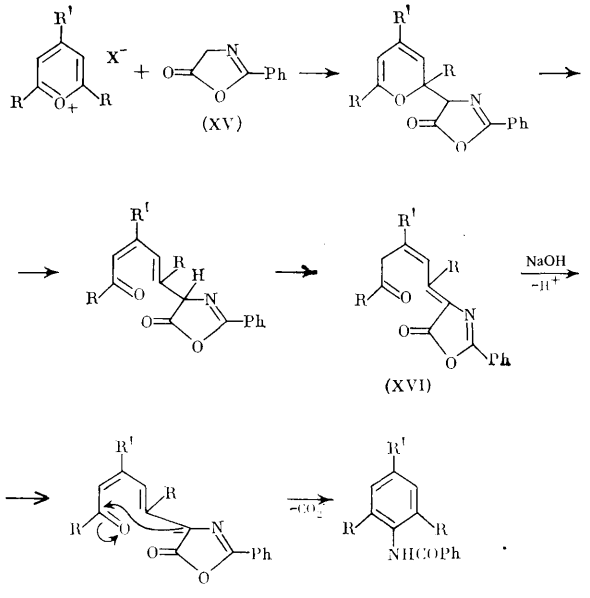
(XIV)

Heteroarylpyrylium salts are also formed when 2- and 4-methoxy-, 2- and 4-methylthio-, and 2- and 4-chloro-pyrylium salts react with nitrogen-containing heterocycles[100,116-121].

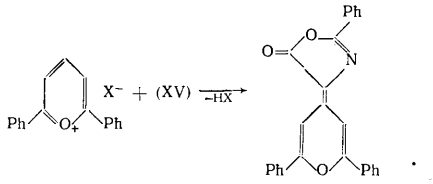
In the reactions of pyrylium salts with enamines containing a tertiary nitrogen atom (NR_2-pyrrolidinyl or NO_2-morpholinyl derivatives) the role of the amino-group split off in the process consists in increasing the nucleophilicity of the double bond[122]:



The interaction of the azlactone (XV) with 2,4,6-trisubstituted pyrylium salts proceeds via nucleophilic attack on the 2-position of the pyrylium ring, leading to the formation of the oxazolinones (XVI). After brief treatment with aqueous alkali, the latter are converted into *N*-benzoylanilines[123]:



The interaction of compound (XV) with 2,6-diphenylpyrylium salts leads to pyranylideneoxazolinone[123]:

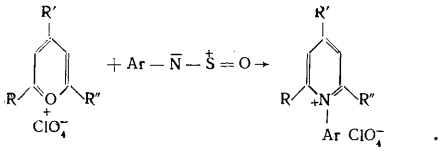


Pyranylidenethiazolinones have been obtained analogously[124].

Thus, nitrogen-containing non-aromatic heterocycles react with pyrylium salts via the most nucleophilic carbon atom.

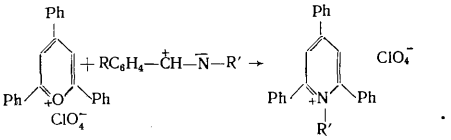
III. REACTIONS WITH COMPOUNDS CONTAINING THE S = N, C = N, AND N_3 GROUPS

The reaction of pyrylium salts with thionylanilines in DMF leads to *N*-arylpyridinium salts[125]. The author suggests that it begins with the addition of thionylaniline to the C(2) atom of the pyrylium ring with subsequent opening of the pyran ring via the intramolecular 1,2-cycloaddition and the elimination of the SO_2 molecule:

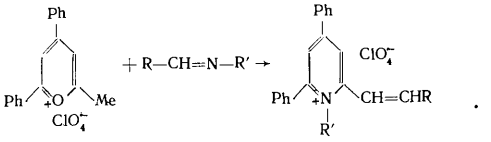


Since the reaction was carried out under conditions ruling out the hydrolysis of thionylanilines, the alternative reaction mechanism involving the hydrolysis of thionylaniline and the reaction of aniline with the pyrylium salt was excluded.

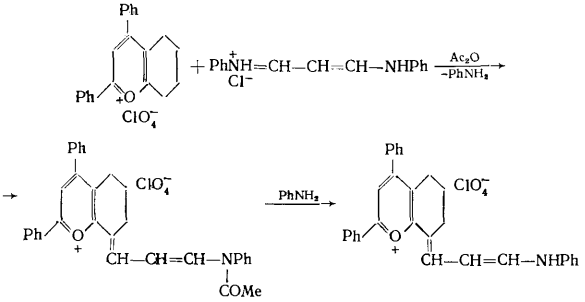
The interaction of TPPP with azomethines in DMF with formation of pyridinium salts[126,127] probably proceeds via a similar mechanism:



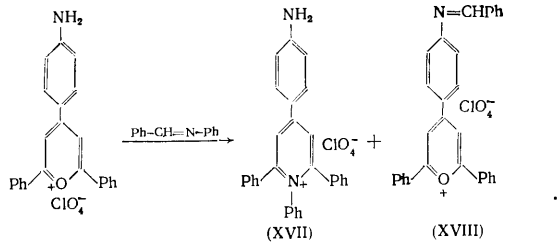
A pyrylium salt with a 2-methyl substituent gives rise to α-styrylpyridinium perchlorate[127]:



The reaction with the dianilide of malonic dialdehyde takes place via the methylene group in the 2-position of the pyrylium cation[128]:



The reaction of 4-(*p*-aminophenyl)pyrylium perchlorate with benzylideneaniline yields two salts—(XVII) and (XVIII)[57]. The reaction takes place preferentially in the 2-position of the initial perchlorate, resulting in the formation of pyridinium salts (XVII), while the benzaldehyde produces the azomethine (XVIII) on reaction with the initial salt[57]:

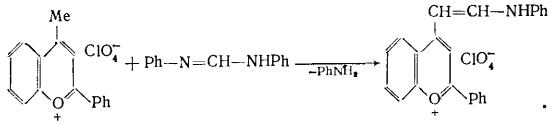


(XVII) (XVIII)

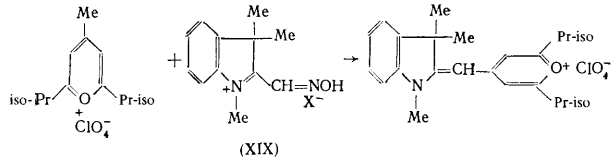
It has been shown separately that compound (XVII) does not react with benzaldehyde under these conditions.

The reaction of substituted 2-benzopyrylium salts with monobenzylidene-*o*-(or *p*-)phenylenediamines proceeds preferentially via the —CH=N— group and not the amino-group[84].

The reaction of 4-methylflavylium perchlorate with diphenylformamidine leads to an aminovinylpyrylium salt[129]:

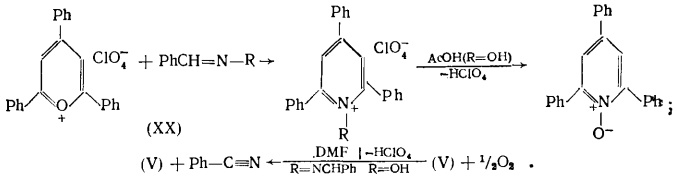


The reaction of 2,6-di-isopropyl-4-methylpyrylium perchlorate with the aldoxime (XIX) also involves the methyl group[72]:



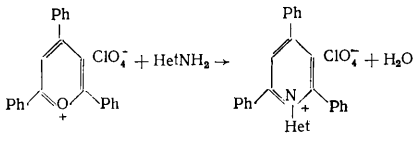
(XIX)

The reactions of TPPP with benzaldoxime (XX, R = OH), benzylidenephenylhydrazine (XX, R = —NHPh), and benzylideneazine (XX, R = —N=CHPh) have been investigated. The reaction with benzaldoxime in acetic acid yielded 2,4,6-triphenylpyridine *N*-oxide, while the reaction with benzylidenephenylhydrazine resulted in the formation of an *N*-anilinopyridinium salt[127]:



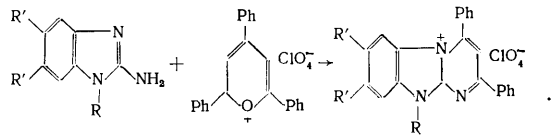
The pyridinium salts formed split off the pyridine (V) in boiling DMF. The reaction with benzylideneazine can be regarded as a method for the synthesis of benzonitrile.

In subsequent years it was found that the reaction of TPPP with heterocyclic amines leads to the formation of *N*-heteroarylpyridinium salts[103,130] (Het = heteroaryl):



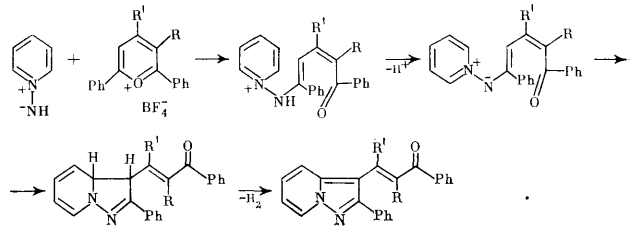
Analogous heteroarylpyridinium salts were obtained from 4-*p*-aminophenyl-2,6-diphenylpyrylium perchlorate[131] and TMPP[60,80,132,133]. However, only the amines whose basicity constants in acetonitrile are $pK_a \geq 5$ react with TMPP via this pathway[103]. The presence of the pyridine nitrogen atom in the heterocycle promotes the elimination of a proton from the methyl group of the pyrylium salt, which, as already mentioned, leads to the formation of a hexamer[103]. Heterocyclic amines in which the basicity of the amino-group is significantly reduced as a result of the significant contribution of the charged resonance form with the positive charge on the nitrogen of the amino-group interact via this pathway.

The condensation of *N*-aminoheterocycles with 2,4,6-substituted pyrylium salts yielded N—N linked heteroarylpyridinium salts[134]. Both nucleophilic centres of the aminoheterocycle molecule (the amino-group and the pyridine nitrogen atom) are involved in the reaction of TPPP with 1-alkyl-2-aminobenzimidazoles, which leads to the formation of pyrimido-[1,2-*a*]benzimidazolium salts[135,136]:

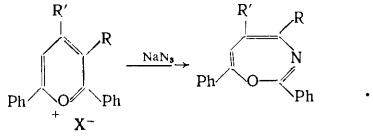


TPPP also forms the condensed pyrimido[1,2-*a*]naphthimidazolium system on reaction with 2-amino-3-benzylnaphtho-[1,2-*d*]imidazole[131,136]. However, the reaction of the above perchlorate with the azomethines of the above heterocyclic amines proceeds similarly to the reactions of benzylideneanilines, which leads to the formation of *N*-heteroarylpyridinium salts[127]. Thus it has been found that, if the heterocyclic amine does not form a quaternary pyridinium salt on reaction with TPPP, it can be obtained from the azomethine derived from the above amine.

The interaction of arylpyrylium salts with *N*-pyridinium imine proceeds via a non-standard pathway, where the 2-position of the pyridine reactant is involved in intramolecular 1,5-dipolar cyclisation. This results in the formation of a derivative of a pyrazolo[1,5-*a*]pyridine[137]:



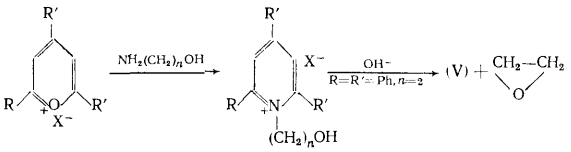
Monocyclic pyrylium salts recyclise to 1,3-oxazepines under the influence of sodium azide[138]:



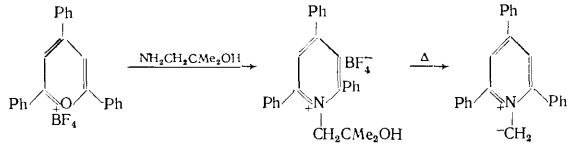
The reaction of 1-benzopyrylium perchlorates with sodium azide, leading to the formation of benzo[*f*]-1,3-oxazepines, proceeds analogously[139].

IV. INTERACTION WITH AMINES CONTAINING OTHER FUNCTIONAL GROUPS

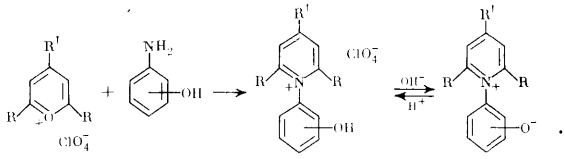
The interaction of pyrylium salts with aliphatic aminoalcohols yielded *N*-hydroxyalkylpyridinium salts[85,140,141]; some of their reactions have been investigated[85,140]:



A novel method has been discovered for the synthesis of 2,4,6-triphenylpyridinium methylide[85]:

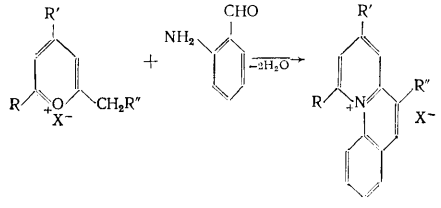


Pyrylium salts readily interact with *p*-, *m*- and *o*-aminophenols and their derivatives with the nitro-group in the *m*-position relative to NH_2, forming 1-hydroxyarylpyridinium derivatives, which are deprotonated on treatment with alkali to O^-–N^+-pyridinium betaines[142,143]:



The symmetrical octahydroxanthylium perchlorate is readily converted into *N*-substituted octahydroacridinium salts by reaction with *o*-, *m*- and *p*-aminophenols and ethanolamine[76].

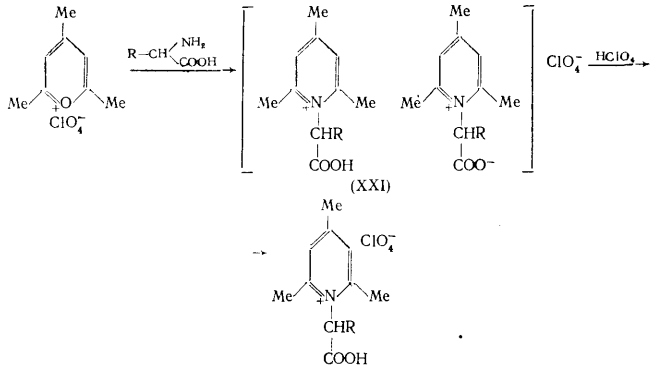
Both functional groups of *o*-aminobenzaldehyde are utilised in its reaction with 2-methyl(or methylene)-substituted pyrylium salts and derivatives of the condensed benzo[*c*]-quinolizinium system were obtained by simple single-stage synthesis[144]:



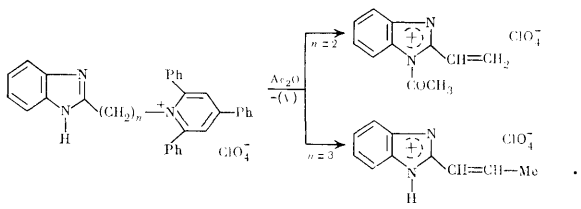
The reaction of pyrylium salts with aromatic aminoacids proceeds with formation of *N*-carboxyphenylpyridinium derivatives[130,145], which are deprotonated by ion-exchange resins, forming stable compounds with a zwitterionic structure[130].

The ethyl esters of glycine, phenylalanine, and glycylglycine readily react with TMPP, TPPP, and 5,6,7,8-tetrahydrobenzopyrylium and *sym*-octahydroxanthylium perchlorates to form *N*-alkoxycarbonyl derivatives of quaternary pyridinium, tetrahydroquinolinium, and octahydroacridinium salts[146,147].

The condensation of TMPP with α-aminoacids and peptides proceeds under less severe conditions than the condensation with their esters, giving rise to the dimeric products (XXI). On treatment with $HClO_4$, the latter are converted into pyridinium salts[145,148]:



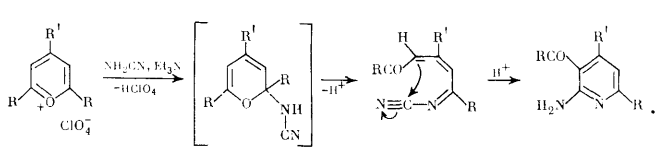
It has been shown that the reaction of TPPP with α-aminoacids does not give rise to condensation products[81]. The interaction of TMPP and TPPP with β-alanine and γ-aminobutyric acid takes place readily, resulting in the formation of the corresponding carboxypyridinium perchlorates. By reaction with *o*-phenylenediamine, the latter were converted into *N*-benzimidazolylalkylpyridinium salts, which underwent thermal decomposition on refluxing in acetic anhydride[81]:



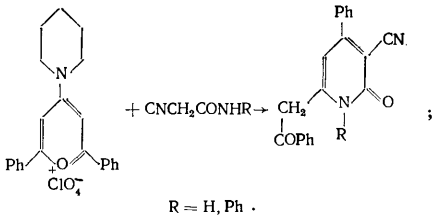
These reactions can be regarded as a simple method of synthesising 2-alkenylbenzimidazoles.

Diaminomonocarboxylic acids (lysine and ornithine) interact with TMPP and TPPP via the ε- or δ-amino-group, forming aminoacids with a pyridinium substituent[149]. On the other hand, pyrylium salts do not react with aminodicarboxylic acids (aspartic and glutamic). The above studies have demonstrated the possibility, in principle, of reactions of pyrylium salts with the free amino-groups of proteins; it has been suggested that the mutagenic action of TMPP is based on this factor[150,151]. The same pyrylium salt has been used as a selective reagent for the chemical modification of α-chymotrypsin[152].

2,4,6-Triarylpyrylium salts interact smoothly with cyanamides in the presence of triethylamine, forming 2-amino-3-aroylpyridines[153]. The reaction with cyanamide belongs to the class of rare reactions in the chemistry of pyrylium salts in which cyanamide behaves initially as the nucleophile and then as the electrophile:

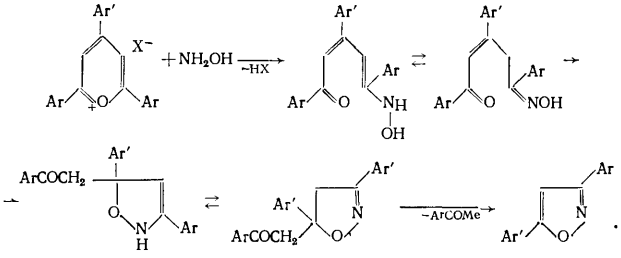


The reaction with cyanoacetamide and cyanoacetanilide in the presence of bases proceeds without the involvement of the cyano-group in the formation of the pyridine ring[58]:



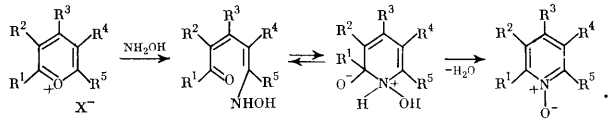
R = H, Ph .

Triarylpyrylium salts react with hydroxylamine in neutral or basic media to form phenacyl derivatives of isoxazolines (XXII), which decompose on heating into acetophenone and 3,5-diphenylisoxazoles[154,155]:



(XXII)

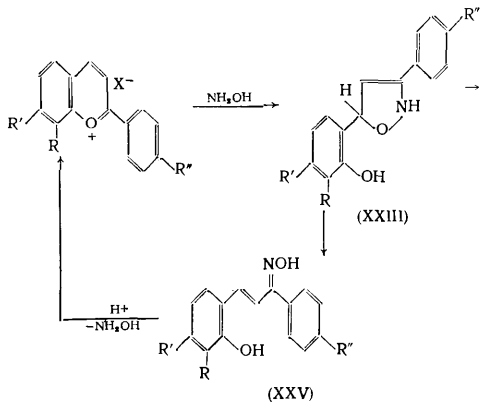
In an acid medium arylpyrylium salts react with hydroxylamine and are converted into the *N*-oxides of arylpyridines[156]:



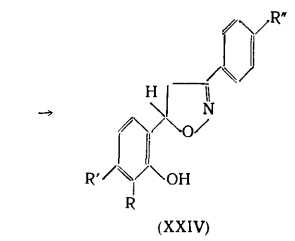
Together with the *N*-oxides, the reactions of 2,4,6-triarylpyrylium salts give rise under these conditions to isoxazolines (XXII) and their oximes. In the presence of even one additional substituent in the 3- or 5-position in the pyrylium ring the reaction proceeds exclusively with formation of pyridine *N*-oxides. The formation of 2,4,6-trimethylpyridine *N*-oxide in the reaction of TMPP with hydroxylamine takes place in both acid and basic media.

The reaction of heteroarylpyrylium salts with hydroxylamine yielded isoxazoles[15,16,157], while isoquinoline *N*-oxide was obtained from 1,3-dimethyl-2-benzopyrylium perchlorate[65].

The reaction of flavylium salts with hydroxylamine leads to *o*-hydroxyphenylisoxazolines (XXIII), which can be made to undergo a thermal rearrangement to isoxazolines (XXIV) or can be converted in acid media into oximes (XXV), which recyclise to the initial flavylium salt by eliminating a hydroxylamine molecule[158]:



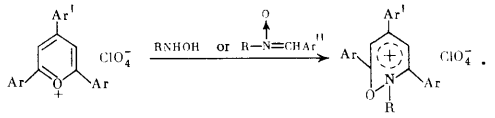
(XXV)



(XXIV)

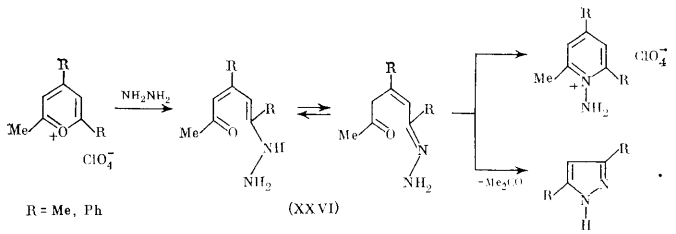
4-Ethoxyflavylium perchlorate reacts with hydroxylamine to form flavone oxime[79].

The reaction of substituted arylhydroxylamines with 2,4,6-triarylpyrylium salts in DMF is accompanied by ring expansion, which leads to the synthesis of a new seven-membered cation with eight π electrons—1,2-oxazepinium[159]:



The same cations have been obtained by the reaction of 2,4,6-triarylpyrylium salts with aldonitrones[159].

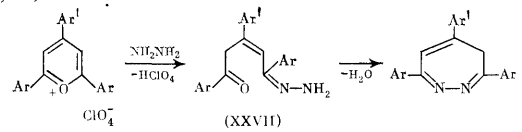
In the presence of a 2-alkyl substituent, pyrylium perchlorates react with hydrazines (1:1 reaction ratio) to form *N*-aminopyridinium salts[160]:



R = Me, Ph (XXVI)

1-Amino-octahydroacridinium[161], 1-amino-2,6-dimethyl-4-(2-benzothiazolyl)pyridinium[16], and 12-amino-11,13-dimethyl[9]-(2,6)pyridinophanium[22] salts have been obtained analogously. The intermediate hydrazone (XXVI) can split off an acetone molecule under mild conditions on treatment with an excess of hydrazine and cyclise to a pyrazole derivative[161].

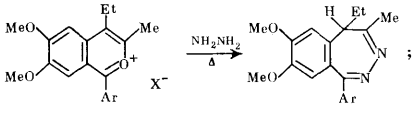
The reaction of arylpyrylium salts with hydrazine is accompanied by ring expansion with formation of 4*H*-1,2-diazepines[57,154,162-164]:



(XXVII)

It has been possible to isolate the intermediate monohydrazone (XXVII), whose intramolecular condensation leads to 1,2-diazepine[165]. 1,2-Diazepines with t-butyl[166] and methyl[58] substituents in the 3- and 7-positions have also been obtained.

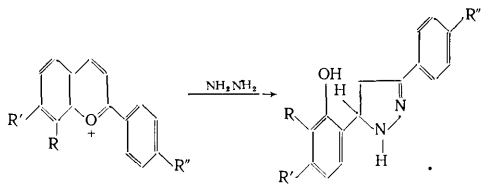
1-Aryl-2-benzopyrylium salts react with hydrazine and are converted into 5*H*-2,3-benzodiazepines[167]:



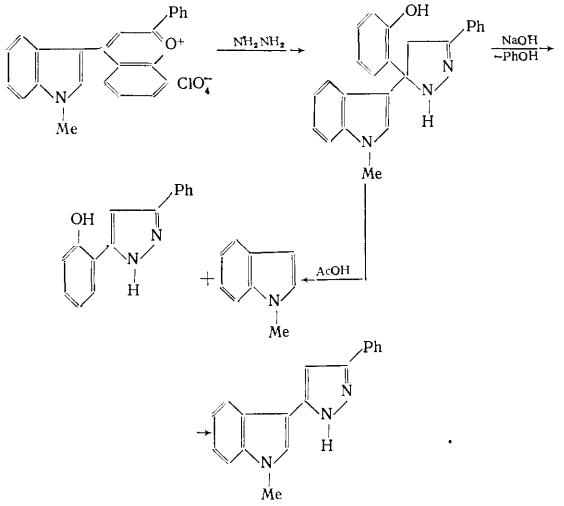
Ar = 3,4-dimethoxyphenyl; X = Cl, Br, HSO_4, ClO_4 .

Flavylium salts with the free 4-position are attacked by hydrazine exclusively in the 2-position. The addition product then isomerises with the opening of the pyran ring and

cyclises to 4,5-dihydro-1*H*-pyrazole[158]:

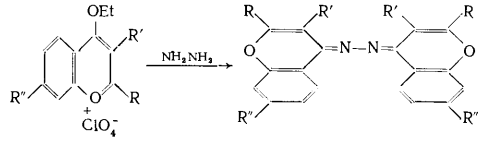


4-Indolylflavylium salts react with hydrazine analogously, but in the presence of a base pyrazoline splits off the phenolic substituent, forming 3-(5-pyrazolo)indole[166]:

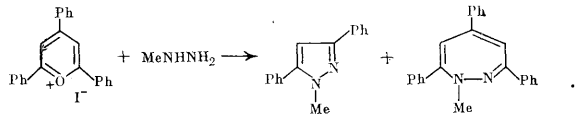


On being refluxed in acetic acid, pyrazoline is cleaved to 1-methylheteroindole and 5-*o*-hydroxyphenyl-3-phenylpyrazole.

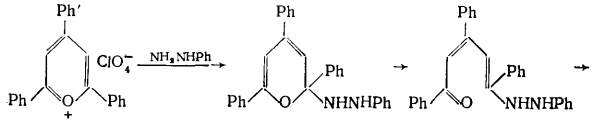
On reaction with hydrazine, 4-ethoxy-1-benzopyrylium salts give rise to chromone azines[79]:

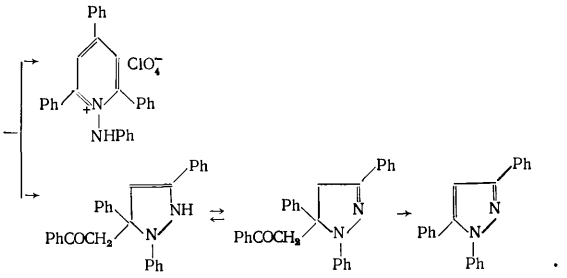


The reaction of 2,4,6-triphenyl- and 2-methyl-4,6-diphenylpyrylium salts with methylhydrazine results in the formation of substituted pyrazoles and a small amount of phenacylmethylpyrazolines, 1-methyl-3,5,7-triphenyl-1*H*-1,2-diazepine having been obtained in 4% yield only from 2,4,6-triphenylpyrylium iodide[168]:

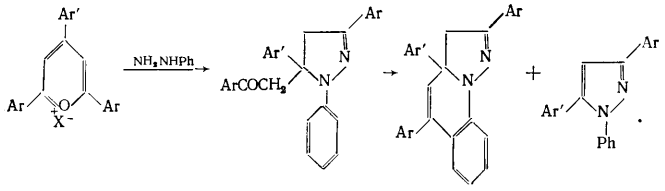


The reaction of 2,4,6-trisubstituted pyrylium salts with an equimolar amount of phenylhydrazine leads to *N*-phenylaminopyridinium salts[169]. On reaction with twice the amount of phenylhydrazine, TPPP recyclises to phenacylpyrazoline, which can split off acetophenone, being converted into pyrazole[154]:





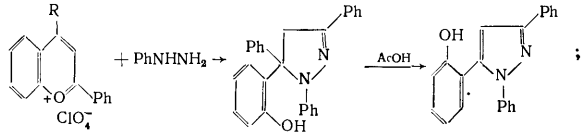
In the presence of a large excess of phenylhydrazine, the resulting phenacylpyrazolines are capable of intramolecular condensation to 4*H*-pyrazolo[2,3-*a*]quinoline[170]:



At the same time the pyrazoline is aromatised to pyrazole, while eliminating acetophenone.

The corresponding pyrazoles have been isolated in the reaction of 4-(2-benzothiazolyl)-2,6-dimethyl-[16] and 4-(1-alkyl-3-indolyl)-2,6-diphenylpyrylium salts[171] with phenylhydrazine.

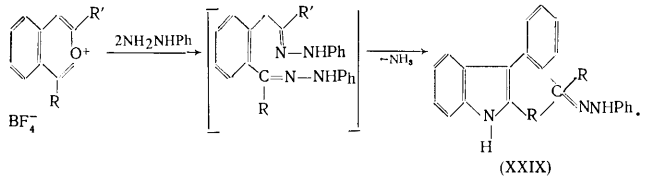
1-Benzopyrylium[166] and pyrylia[2,3-*c*]indole salts[157] react with phenylhydrazine to form pyrazolines, for example (XXVIII):



(XXVIII)

R = 1-methyl-3-indolyl.

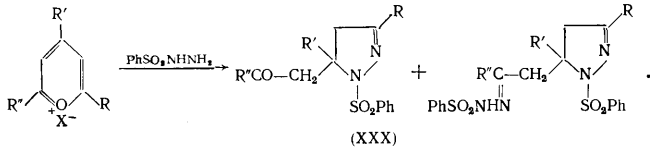
The reaction of 2-benzopyrylium salts with phenylhydrazine gives rise to substituted indoles (XXIX), probably via an intermediate bisphenylhydrazone, as in the Fischer synthesis of indoles[49]:



(XXIX)

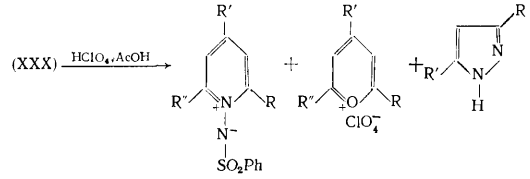
Examples of the conversion of pyrylium salts into 1-phenyl-1*H*-1,2-diazepines are as yet unknown.

Benzenesulphonyl hydrazide reacts with arylpyrylium salts to form pyrazolinylacetophenones (XXX) or a mixture of the latter with their benzenesulphonylhydrazones[172]:



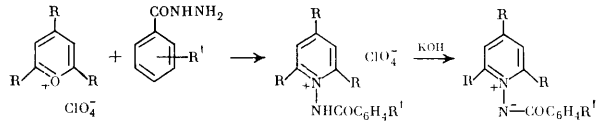
(XXX)

It is of interest that treatment of the pyrazolines (XXX) with $HClO_4$ in acetic acid can effect their recyclisation either to *N*-pyridiniabenzenesulphimide or a pyrylium salt, depending on the nature of the aryl substituent[173]:

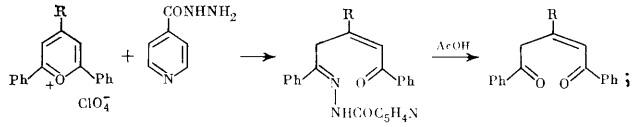


For R′ = R″ = Ph and R = *p*-$NO_2C_6H_4$, a mixture of three products is obtained, for R′ = R″ = Ph and R = *p*-BrC_6H_4, only the pyrylium salt is formed, and for R″ = Me and R = R′ = *p*-$NO_2C_6H_4$, the only product is a betaine.

The reactions of substituted benzoyl hydrazides with pyrylium salts proceed similarly to the reactions with aromatic amines, giving rise to the formation of 1-acylaminopyridinium salts, whose treatment with alkali leads to acyliminopyridinium betaines[161,174,175]:



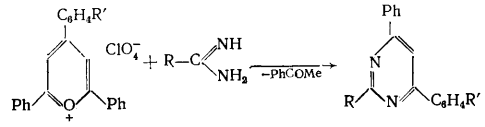
When arylpyrylium perchlorates are refluxed in DMF with twice the amount of benzoyl or isonicotinoyl hydrazide, pentene-1,5-dione monobenzoyl- or monoisonicotinoylhydrazones are formed and are then hydrolysed to the 1,5-diketones on refluxing in acetic acid[171]:



R = 1-benzyl-3-indolyl, 1-methyl-3-indolyl, or phenyl.

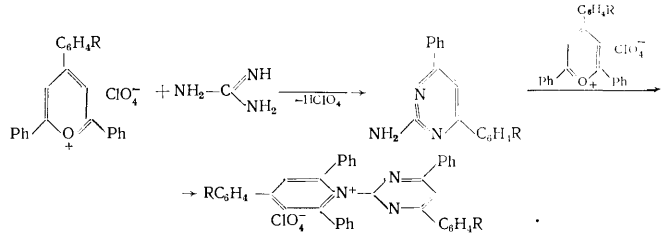
V. REACTIONS WITH POLYFUNCTIONAL AMINES CONTAINING THE N—C—N GROUP

It has been observed recently that the reactions of 2,4,6-triarylpyrylium perchlorates with amidines involve both amino-groups of the latter, which leads to the formation of 2,4,6-triarylpyridines[176,177]:

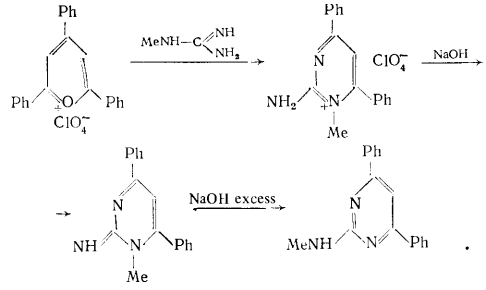


Pyrylium salts unsubstituted in the 4-position interact with amidines similarly, forming 2,4-diarylpyrimidines[177]. Methylpyrylium salts are not converted into pyrimidines on treatment with amidines.

The recyclisation of 2,4,6-triarylpyrylium perchlorates on reaction with guanidine leads to the intermediate 2-aminopyrimidines, which react with the initial pyrylium salt[178,179]:

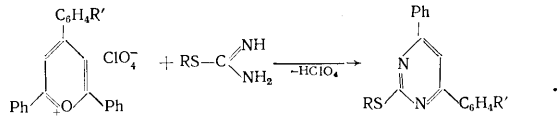


When the same pyrylium salts react with methylguanidine, the pyrylium cation is attacked preferentially by the more basic methylamino-group of the nucleophile. The structure of the resulting unstable 2-iminodihydropyrimidine has been confirmed by the Dimroth rearrangement to 2-methylamino-4,6-diphenylpyrimidine[179]:



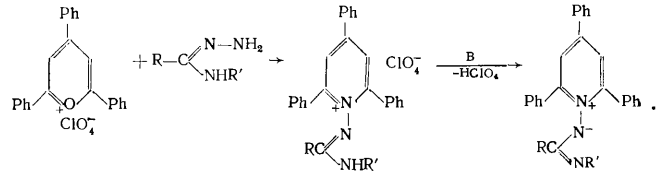
TMPP and TPPP react with sulphanilylguanidine via one amino-group of the guanidine fragment, forming the corresponding pyrimidinium salts[179]. The formation of the pyrimidine ring might have been expected also in the reaction of pyrylium salts with urea or thiourea. However, the interaction of these compounds and of *N*-substituted ureas with TPPP in DMF leads to pyridine (V)[180].

In contrast to ureas and thiourea, S-substituted isothioureas react readily with pyrylium salts, forming 2-alkylthio-4,6-diarylpyrimidines[180,181]:

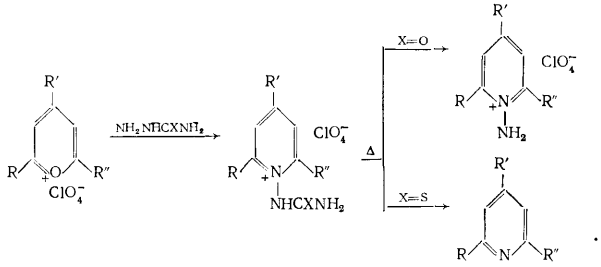


2-Methyl-4,6-diphenylpyrylium perchlorate and TMPP are converted into the corresponding pyridines by reaction with *S*-benzylisothiourea. Evidently, the electrophilicity of the C(4) atom in these salts is insufficient for cyclisation to pyrimidine.

In the reaction with TPPP under mild conditions, amidrazones form 2,4,6-triphenylpyridinium salts, which are readily deprotonated in the presence of bases to substituted pyridinium *N*-ylides[182,183]:

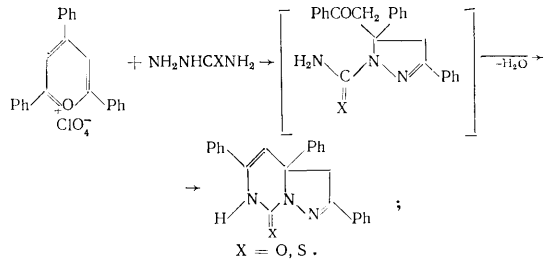


The reactions of 2,4,6-trisubstituted pyrylium salts with semi- and thiosemi-carbazides in ethanol involve one amino-group of the hydrazine fragment and lead to *N*-carbamido- and *N*-thiocarbamido-pyridinium salts[180]:



N-Carbamidopyridinium salts undergo thermal cleavage in DMF, which constitutes a convenient method of preparing *N*-aminopyridinium salts. *N*-Thiocarbamidopyridinium salts undergo thermal degradation in boiling DMF via a different mechanism involving the elimination of the corresponding pyridines[180].

When TPPP is refluxed with semi- and thiosemi-carbazides in DMF, the reaction involves the second amino-group of the hydrazine fragment of the latter and a pyrazoline ring is formed. Subsequent intramolecular condensation of the amino-group with the carbonyl group of the phenacyl substituent completes the formation of a new bicyclic system—7-hydroxy(mercapto)-2,3a,5-triphenyl-3*H*-pyrazolo[1,5-c]-pyrimidine[184]:



Thus the interaction of arylpyrylium and 2-benzopyrylium salts with nitrogen-containing nucleophiles takes place via the attack of the latter on the carbon next to the oxygen atom and subsequent recyclisation if this is possible. In pyrylium salts with functional and alkyl substituents and also in the salts with an unsubstituted electron-deficient position, an additional electrophilic centre appears and the reactions proceed via one pathway or another depending on the reactant and the process conditions.

Under the influence of the condensed benzene ring, 1-benzopyrylium salts lose their ability to exchange the heteroatom.

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The data presented in this review demonstrate the likely usefulness of pyrylium salts as synthons in organic chemistry, since numerous aliphatic, aromatic and heterocyclic functional derivatives as well as pyridines, pyridinium salts, pyrazoles, isoxazoles, pyrimidines, diazepines, 1,3-oxazepines, 1,2-oxazepinium salts, and various condensed heterocyclic compounds can be obtained from them.

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Preparation and Properties of Carbodi-imides and Cyanamides Containing Silicon, Germanium, Tin, and Lead

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Information on methods of preparation and properties of carbodi-imides and cyanamides containing Group IVB elements is summarised and systematised. Reaction schemes are discussed, and several aspects of their practical application are examined. A list of 221 references is included.

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I. INTRODUCTION

Carbodi-imides and cyanamides are genetically interrelated and are functionally closely similar, but for compounds containing Group IVB elements isomeric transitions are observed between the two groups of compounds. In many cases methods of preparation and reactivities are the same. This is why hetero-organic cyanamides and carbodi-imides are considered together in this Review.

Progress in the chemistry and application of organic carbodi-imides has been repeatedly and exhaustively discussed in reviews[1-3], but information on hetero-organic carbodi-imides and cyanamides has not been fully systematised. There exist only a survey of organosilicon carbodi-imides and cyanamides[4] and a review[5] which considers organotin carbodi-imides together with other compounds containing tin–nitrogen bonds. A considerable number of papers have appeared recently which, together with earlier information, are worthy of special discussion.

The present Review aims to systematise published information on the preparation, reactivity, physicochemical properties, and applications of carbodi-imides and cyanamides containing silicon, germanium, tin, and lead. Monographs, periodical literature, and patents appearing up to 1980 are covered.

II. METHODS OF PREPARATION

1. Interaction of Cyanamide and its Derivative with Hetero-organic Compounds

The first example of a hetero-organic carbodi-imide, disilylcarbodi-imide, was obtained[6] in 25% yield by passing gaseous iodo- or bromo-silane over silver cyanamide, in conformity with the general equation

$$Ag_2N{-}C{\equiv}N + R_3MX \rightarrow AgX + R_3M{-}N{=}C{=}N{-}MR_3 \qquad (1)$$

in which M = Si, R = H, and X = Br, I. It was originally supposed that the product was the cyanamide $N{:}C.N(SiH_3)_2$. However, infrared and Raman spectral data[7-9] and also investigation of a deuterated derivative[8] showed that it had the carbodi-imide structure $H_3SiN:C:NSiH_3$. The yield of bistrimethylsilylcarbodi-imide obtained by this reaction (M = Si, R = CH_3, X = Cl) is not appreciably influenced by use of a solvent[10-12]. More severe conditions are required in the absence of a solvent (170 °C for 5 h, yields 90%) [10,11] than in ether (20 °C for 10 h, yield 80%) [12] or in benzene (yield 90%).[13]

The potential danger of explosion with dry silver cyanamide creates great difficulties in carrying out preparations[6,11,14,15]. Individual organosilicon carbodi-imides have therefore been obtained from the corresponding chlorosilanes in boiling benzene or in acetonitrile [Eqn.(1): M = Si, R_3 = $(C_2H_5)_3$, $(C_3H_7)_3$, $(C_6H_{13})_3$, $CH_3(C_6H_5)_2$, $(CH_3)_2C_6H_5$, $(C_6H_5)_3$, $(C_6H_5)_2CH_2:CH$, $(C_2H_5O)_3$; X = Hal]. The reaction in acetonitrile is accelerated by adding small quantities of water[15], but the catalytic effect decays rapidly.

Use of a mixture of two different trialkyl- or triaryl-chlorosilanes yields three different carbodi-imides[15]:

$$Me_3SiCl + Ph_3SiCl + Ag_2NCN \xrightarrow[-AgCl]{} Me_3SiN{=}C{=}NSiMe_3 + Me_3SiN{=}C{=}NSiPh_3 + Ph_3SiN{=}C{=}NSiPh_3$$

However, the unsymmetrical carbodi-imide cannot be isolated, because it disproportionates when distilled[15]:

$$Me_3SiN{=}C{=}NSiPh_3 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + Ph_3SiN{=}C{=}NSiPh_3$$

Silver cyanamide is used to obtain several symmetrical organosilicon and organogermanium carbodi-imides of general formula $C[:NM(CH_3)_nH_{3-n}]_2$ (M = Si, Ge; $n = 0-3$). The corresponding chloro- or iodo-silanes and bromo- or iodo-germanes have been used as the second reactant[16]. Reaction (1) is suitable also for the preparation of symmetrical organotin carbodi-imides[17-19].

Application of an analogous reaction to silver cyanamide has enabled polymeric carbodi-imides containing silicon to be synthesised from dialkyl- and diaryl-dichlorosilanes[20]. A tetramer of dibutylbiscarbodi-imidostannane has been obtained similarly from di-n-butyltin dichloride[21]:

$$n Ag_2NC{\equiv}N + nRR'MCl_2 \rightarrow -(-MRR'-N{=}C{=}N-)_n- + 2nAgCl$$

M = Si; RR' = Me_2, Ph_2, MePh, MeVin, $(EtO)_2$;
M = Sn; RR' = Bu_2; $n = 4$.

In view of the high cost and explosiveness of silver cyanamide it is advisable to replace it by sodium, calcium, zinc, or lead cyanamide[15,16,22-24]. Thus bistrimethylsilylcarbodi-imide can be obtained[22] in 76% and 46% yields by passing trimethylchlorosilane through technical disodium and calcium cyanamides respectively in a lithium–potassium chloride melt:

$$Na_2NC{\equiv}N + R_3MX \rightarrow R_3MN{=}C{=}NMR_3 + NaCl \qquad (2a)$$

$$M'NC{\equiv}N + R_3MX \rightarrow R_3MN{=}C{=}NMR_3 + M'X_2 \qquad (2b)$$

where M = Si, M′ = Ca, R = CH_3, X = Cl. It has recently been shown that carbodi-imides can be obtained in high yields (80–90%) without the use of molten salts by a modified technique[6] involving passing gaseous iodides over anhydrous lead cyanamide at 25 °C [Eqn.(2b): M = Si, Ge; M′ = Pb; $R_3 = (CH_3)_nH_{3-n}$; $n = 0-3$; X = I].[16–24] Bistrimethylsilyl- and bistrimethylgermyl-carbodi-imides have been prepared by the action of trimethylchlorosilane and trimethylbromogermane respectively on lead cyanamide at 100 °C for 5 h [Eqn.(2b): M = Si, Ge; M′ = Pb; R = CH_3; X = Cl, Br].[16] The action of triphenyltin iodide on disodium cyanamide [in benzene at 80 °C for 23 h; Eqn.(2a): M = Sn, R = C_6H_5, X = I] [25] and on monosodium cyanamide[26] and that of triethyltin chloride on the latter (in ether at 0–25 °C) [27] give high yields of the corresponding organotin carbodi-imides:

$$Et_3SnCl + NaNHC{\equiv}N \xrightarrow{-NaCl} Et_3SnNHCN \rightarrow Et_3SnN{=}C{=}NSnEt_3 + H_2NCN$$

The above reactions can be successfully used to synthesise various symmetrical and unsymmetrical hetero-organic carbodi-imides and the isomeric cyanamides. Interaction of organic halides of silicon, germanium, tin, and lead with appropriate cyanamide derivatives of silver, potassium, calcium, barium, or strontium has yielded in particular $R_3SiN:C:NC_6H_5$ (R = CH_3, C_6H_5),[28] $(C_6H_5)_2Si(N:C:NC_6H_5)_2$,[28] $(C_6H_5)_3SnNCNC{\vdots}N$,[29] $R_3SnN(C_6H_5)C{\vdots}N$ (R = CH_3, C_6H_5),[30] $(C_2H_5)_3SnOC(CH_3)NCN$,[31] $R_2Sn(OCR'NCN)_2$ (R = CH_3, C_2H_5, C_4H_9, C_6H_5, $C_6H_5CH_2$; R′ = CH_3, C_6H_5),[31] $[(C_4H_9)_3SnS]_2C:N.C{\vdots}N$,[32] $(C_4H_9)_2Sn\langle S \rangle C:N.C{\vdots}N$,[32–34] $R_3MN(CN)_2$ (M = Ge, Sn, Pb; R = CH_3, C_6H_5),[35–37] and $R_2Sn[N(CH)_2]_2$ (R = CH_3, C_6H_5).[36,37].

N-Phenyl-*N*′-trimethyl[phenyl]silylcarbodi-imides can also be synthesised in 55–79% yields from phenylcyanamide[28,38–41]. The same method has since been used to obtain several other unsymmetrical organosilicon carbodi-imides[4,38–41]:

$$R_3MX + R'NHC{\equiv}N + Et_3N \rightarrow R'N{=}C{=}NSiR_3 + Et_3N{\cdot}HX$$
M = Si; R = Me, Ph; R′ = Me, Et, t-Bu, Ph, Ph_3C, EtOCO; X = Cl.
M = Sn, R = Ph, R′ = Ph_3C, X = I .

The compounds $RN:C:NSi(CH_3)_3$ are found to exist in tautomeric equilibrium with the corresponding cyanamides $RN(C{\vdots}N)Si(CH_3)_3$.[4,40,41]

Cyanamide itself also proved useful for the synthesis of carbodi-imides[12]. Thus with trimethylchlorosilane in the presence of triethylamine in ethereal solution (at ~20 °C for 1 h) a high yield of bistrimethylsilylcarbodi-imide is formed:

$$H_2NC{\equiv}N + 2R_3MX + 2Et_3N \rightarrow 2Et_3N{\cdot}HX + R_3MN{=}C{=}NMR_3 \quad (3)$$
M = Si, R = Me, X = Cl .

The first organogermanium carbodi-imide, bistributylgermylcarbodi-imide, was obtained by heating an ethereal solution of cyanamide, sodium ethoxide, and tributylgermanium chloride (yield 24%).[43] When triphenylgermanium bromide is heated with cyanamide in the presence of triethylamine in isopropyl ether, a 66% yield of bistriphenylgermylcarbodi-imide is obtained [Eqn.(3): M = Ge, R = C_6H_5, X = Br].[44]

Organotin carbodi-imides have been obtained similarly. Thus heating ethereal solutions of triethyltin chloride or triphenyltin iodide with cyanamide and triethylamine gave high fields of bistriethyl[phenyl]stannylcarbodi-imides respectively[17,25] [Eqn.(3): M = Sn, R = C_2H_5, C_6H_5; X = Cl, I].

Silylation of cyanamide with a mixture of trimethylchlorosilane and lithium in oxolan also yields bistrimethylsilylcarbodi-imide. When the duration of the reaction is increased, however, tristrimethylsilylamine and trimethylsilyl cyanide are formed[42]:

$$H_2NC{\equiv}N + 2Me_3SiCl + 2Li \xrightarrow[0-10^\circ]{\text{oxolan}} Me_3SiN{=}C{=}NSiMe_3 + 2LiCl + H_2$$
$$Me_3SiN{=}C{=}NSiMe_3 + 2Me_3SiCl + 2Li \xrightarrow{\text{oxolan}} (Me_3Si)_3N + Me_3SiCN + 2LiCl .$$

The next step in simplifying the preparation of heteroorganic carbodi-imides was to use organoelementary oxides and hydroxides as metallating agents, which made it unnecessary to introduce acceptors for hydrogen chloride and ultimately diminished the number of chemical operations. Furthermore, the yields of the final products remained high, and in isolated cases approached theoretical. Thus reaction of cyanamide with bistriethylgermyl[45], bistriethylstannyl[27,46], bistributylstannyl[47], bistriphenylstannyl[25,48], and bistris(trimethylsilylmethyl)stannyl[49] oxides gives the corresponding carbodi-imides in 80–95% yields:

$$R_3MOMR_3 + H_2NCN \rightarrow R_3MN{=}C{=}NMR_3 + H_2O$$
M = Ge, R = Et; M = Sn, R = Et, Bu, Ph, CH_2SiMe_3 .

Cyanamide reacts similarly with tin- and lead-containing hydroxides[27,46,49]:

$$R_3MOH + H_2NCN \rightarrow R_3MN{=}C{=}NMR_3 + H_2O$$
M = Sn, R = Et, Ph; M = Pb, R = Ph .

Despite the simplicity of the scheme, the reaction mechanism is quite complicated. It is assumed (in the case of organotin compounds[27]) that an organometallic cyanamide is formed initially, whose disproportionation yields the corresponding carbodi-imide and cyanamide:

$$R_3SnOSnR_3 + H_2NCN \rightarrow R_3SnNHC{\equiv}N + H_2O \quad (4a)$$

$$R_3SnNHCN \rightarrow R_3SnN{=}C{=}NSnR_3 + H_2NCN \quad (4b)$$

$$H_2NCN \rightarrow HN{=}C(NH_2)NHCN . \quad (4c)$$

It was shown later that trimethyltin, tributyltin[50], and triphenyltin[25] cyanamides could be obtained in conformity with Eqns.(4a: R = C_4H_9, C_6H_5) and

$$R_3MOH + H_2NCN \rightarrow R_3MNHC{\equiv}N + H_2O \quad (5)$$

(M = Sn, R = CH_3), and then underwent disproportionation.

Another possible mechanism in that the metallating agent may interact with the active (acidic) hydrogen atom present in the trialkyltin cyanamide $R_3SnNHCN$ formed initially, and the resulting bistrialkylstannylcyanamide may then isomerise to the corresponding carbodi-imide. Metallation may also occur with migration of the reaction centre, when the bistrialkylstannylcarbodi-imide is formed directly.

Reaction (5) has been used also for the preparation of trimethyl-lead cyanamide with alcohol as solvent[51].

Attempts to obtain silicon-containing cyanamides of type $R_3SiNHCN$ have proved unsuccessful. Thus, instead of the expected mono- and bis-trimethylsilylcyanamides, bistrimethylsilylcarbodi-imide was isolated independently of the reaction conditions[12]. It has now been shown that existence is possible only for substituted organosilicon cyanamides of type $(CH_3)_3SiN(CN)COOC_2H_5$ [52] and $RR^1R^2SiCH_2NR^3C{\vdots}N$ (R = CH_3, Cl; R^1, R^2, R^3 = Alk, Ar, AlkO).[53] Cyanamides $(CH_3)_3SiNRC{\vdots}N$ have also been synthesised, in tautomeric equilibrium with the corresponding carbodi-imides $(CH_3)_3$.SiNCNR (R = Alk, Ar).[4,40,41,54,67,68].

Cyanamide reacts with methoxytributyltin to give an 89% yield of bistributylstannylcarbodi-imide[55], the reaction being regarded as reversible:

$$H_2NCN + Bu_3SnOMe \rightleftarrows MeOH + Bu_3SnN{=}C{=}NSnBu_3 .$$

When methoxytributyltin is replaced by tributyltin isocyanate, reaction occurs only in the presence of triethylamine (at 80 °C for 48 h), and up to 68% yields of the carbodi-imide are

obtained[56]:

$$Bu_3SnN{=}C{=}O + H_2NC{\equiv}N \xrightarrow{Et_3N} Bu_3SnN{=}C{=}NSnBu_3 + HNCO .$$

A method has been proposed[57] for preparing disilylcarbodi-imide from cyanamide:

$$H_2NCN + H_3SiPH_2 \rightarrow H_3SiN{=}C{=}NSiH_3 + PH_3$$
$$H_2NCN + (H_3Si)_2S \rightarrow H_3SiN{=}C{=}NSiH_3 + H_2S .$$

Cyanamide is silylated also by hexamethyldisilazane, when the yield of bistrimethylsilylcarbodi-imide is 95%:[58,59]:

$$H_2NCN + (M_3Si)_2NH \rightarrow Me_3SiN{=}C{=}NSiMe_3 + NH_3 .$$

This method—the reaction of cyanamide and its derivatives with hetero-organic compounds—nevertheless has several important disadvantages: cyanamide is difficultly accessible, toxic, and unstable, its silver salts are explosive, large quantities of solvents are used, and in several cases the yields are comparatively low. They are almost all eliminated by replacing cyanamide by its dimer, dicyanodiamide[58-62]. The procedure is to heat the latter to 110–200 °C with a hetero-organic compound containing a bond between the heteroatom and nitrogen or oxygen, and gives very high yields of carbodi-imides containing silicon, germanium, or tin:

$$HN{=}C(NH_2)NHCN \rightarrow \begin{cases} \xrightarrow{(Me_3Si)_2NH} Me_3SiN{=}C{=}NSiMe_3 + NH_3 \\ \xrightarrow{Et_3GeNEt_2} Et_3GeN{=}C{=}NGeEt_3 + Et_2NH \\ \xrightarrow{(Bu_3Sn)_2O} Bu_3SnN{=}C{=}NSnBu_3 + H_2O \end{cases} .$$

Silylating agents used in the preparation of bistrimethylsilylcarbodi-imide have been hexamethyldisilazane, silylamines of the type $Z[NHSi(CH_3)_3]_2$ ($Z = CH_2C_6H_4CH_2$, $CH_3C_6H_3$), *N*-cyclohexyltrimethylsilylamine, tristrimethylsilylmelamine, and tristrimethylsilyl cyanurate[58-62]. Polysilylcarbodi-imides have been synthesised from dicyanodiamide and polysilazanes[62], and *N*-tributylplumbylcarbodi-imide has been obtained by the use of tributyl-lead hydroxide as metallating agent[51].

In conclusion we may state that reactions of the above type have the greatest preparative value at present because of their universality.

2. Preparation from Compounds containing Heteroatom–Nitrogen Bonds

The reactions involved comprise mainly those of cyanogen halides with silicon-containing amino-derivatives. In the preparation of organosilicon carbodi-imides cyanogen halides react with primary and secondary silylamines under milder conditions[4,63-68] than with the tertiary amines (at 50–100 and 200 °C):

$$Et_3SiNH_2 + ICN \rightarrow Et_3SiN{=}C{=}NSiEt_3 + NH_4I$$
$$(Me_3Si)_2NH + XCN \rightarrow Me_3SiN{=}C{=}NSiMe_3 + Me_3SiX + NH_4X$$
$$X = Cl, Br$$
$$(Me_3Si)_3N + ClCN \rightarrow Me_3SiN{=}C{=}NSiMe_3 + Me_3SiCl .$$

With organosilicon amines of types $RNHSi(CH_3)_3$ [R = CH_3, C_2H_5, iso-C_3H_7, $(CH_3)_3C$, C_6H_5] [40,60] and $RN[Si(CH_3)_3]_2$ (R = CH_3, C_4H_9, $CH_2{:}CHCH_2$) [4,40,66-68] cyanogen chloride forms unsymmetrical carbodi-imides in tautomeric equilibrium with the corresponding cyanamides:

$$RN(SiMe_3)_2 + ClCN \xrightarrow[-Me_3SiCl]{20-35^\circ} RN{=}C{=}NSiMe_3 \rightleftarrows Me_3Si(R)N{-}C{\equiv}N . \quad (6)$$

The action of cyanogen chloride on silicon-containing amides of carboxylic acids gives high yields of *N*-acyl-*N'*-trimethylsilylcarbodi-imides[4,66-68]:

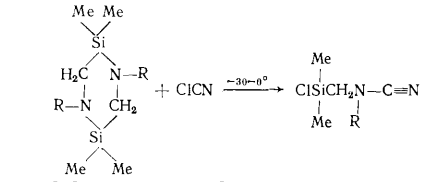
$$RC(O)N(SiMe_3)_2 + ClCN \xrightarrow{20-50^\circ} RC(O){=}N{=}C{=}NSiMe_3 + Me_3SiCl$$
$$R = Me, Ph .$$

These products have been obtained also by cross synthesis—reaction between acyl chlorides and bistrimethylsilylcarbodi-imide—and are shown by infrared, nuclear magnetic resonance, and mass spectral data to exist in the three tautomeric forms[4,66-68]

$$PhC(O){=}N{-}C{=}NSiMe_3 \rightleftarrows PhC(O){-}N(SiMe_3){-}C{\equiv}N \rightleftarrows PhC(OSiMe_3){=}N{-}C{\equiv}N \quad (7)$$
(a) (b) (c)

Cyanamides containing silicon and an organic function were first obtained by the reaction of cyanogen chloride with linear and cyclic *CN*-disilylalkylamines[53,66]:

$$MeSi(R')(R'')CH_2NSiMe_3 + ClCN \xrightarrow{20-60^\circ} MeSi(R')(R'')CH_2N{-}C{\equiv}N + Me_3SiCl$$



$$+ ClCN \xrightarrow{-30-0^\circ} ClSi(Me)(R)CH_2N{-}C{\equiv}N$$

(R, R' = Me, MeO, EtO; R'' = iso-Pr and iso-Bu, Ph).

An organosilicon cyanamide is formed also by the action of cyanogen chloride on *NN*-dimethyl-*N'*-trimethylsilylhydrazine[69]:

$$Me_2N{-}NHSiMe_3 + ClCN \xrightarrow{-Me_3SiCl} Me_2N{-}N(SiMe_3){-}C{\equiv}N .$$

Silylamines of types $(CH_3)_2NSiH_3$, $CH_3N(SiH_3)_2$, and $(H_3Si)_3N$ apparently[70] do not form silylcarbodi-imides on treatment with cyanogen chloride.

Unsymmetrical carbodi-imides containing silicon, germanium, or tin can be obtained also from organometallic amines. Investigation of the reaction of benzoyl-t-butylcarbodi-imide with amines of types $(CH_3)_3M.N(CH_3)_2$ (M = Si, Ge, Sn) and $[(CH_3)_3M]_2NCH_3$ (M = Si, Sn) established[71,72] that the equimolecular insertion products when heated to 150 °C decomposed with the formation of unsymmetrical organo-silicon and -germanium carbodi-imides (yields 68–82%):

$$PhC(O)N{=}C{=}NCMe_3 + Me_3MN(R){-}Me \rightarrow$$
$$\rightarrow PhC(O)N(R){-}C(MMe_3){=}NCMe_3 \xrightarrow{150^\circ} Me_3MN{=}C{=}NCMe_3 + PhC(O)N(R){-}Me$$
$$M = Si, R = Me, Me_3Si; M = Ge, R = Me .$$

High yields of unsymmetrical organotin carbodi-imides have been obtained[73] by the action of isothiocyanates on tristrimethylstannylamine:

$$(Me_3Sn)_3N + RN{=}C{=}S \rightarrow R{-}N{=}C{=}NSnMe_3 + (Me_3Sn)_2S$$
$$R = t\text{-}Bu, C_6H_{11}, Ph .$$

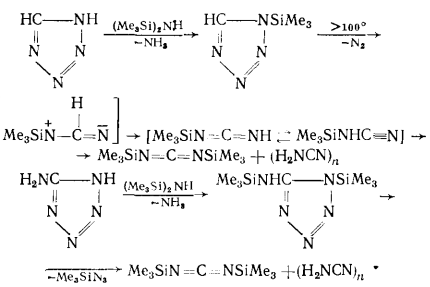
Bistrimethylsilylcarbodi-imide can be obtained in 80% yield by reaction between heptamethyldisilazane and *N*-sulphinylcyanamide[74-76], in ether at −70 °C since the latter reactant

decomposes explosively:

$$N{\equiv}C{-}N{=}S{=}O + (Me_3M)_2NMe \rightarrow$$
$$\rightarrow Me_3MN{=}C{=}NMMe_3 + MeN{=}S{=}O$$
$$M = Si, Sn .$$

Bistrimethylstannylcarbodi-imide has been obtained similarly[76].

Bistrimethylsilylcarbodi-imide can be isolated as either the main product or a by-product when certain compounds are heated with hexamethyldisilazane. Thus a high yield is obtained from tetrazoles[76-82]:



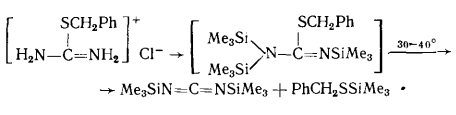
Heating hexamethyldisilazane with the polyurethane $[CONHRCH_2RNHCO_2CH_2CH_2O]_n$ ($R = p\text{-}C_6H_4$) at 197 °C for 21 h yields a mixture of bistrimethylsilylcarbodi-imide, trimethylsilyl isocyanate, hexamethyldisiloxane, and other products[83-85]. Bistrimethylsilylcarbodi-imide is formed as a by-product in the thermolysis of a mixture of the isocyanate and hexamethylenediamine[86,87]. It is obtained in good yield (85–90%) by heating isothiocyanatobistrimethylsilylamine[88]:

$$(Me_3Si)_2N{-}N{=}C{=}S \xrightarrow{110^\circ} Me_3SiN{=}C{=}NSiMe_3 + S_8 .$$

3. Reactions with Urea and Thiourea

Substituted ureas, thioureas, and isothioureas are the traditional and principal starting materials for the preparation of carbodi-imides[1,3]. However, the usual methods of dehydration of hetero-organic ureas and elimination of hydrogen sulphide from hetero-organic thioureas are unacceptable owing to the great reactivity of the resulting hetero-organic carbodi-imides[1]. Furthermore, urea and thiourea cannot be completely silylated with trimethylchlorosilane or hexamethyldisilazane[89]. An attempt to silylate urea and biuret with triethylsilane[90] was also unsuccessful, owing to the low yields and the difficulty of separating the products (triethylsilyl isocyanate, bistriethylsilylcarbodi-imide, and bistriethylsilyl ether). Therefore this route to the synthesis of hetero-organic carbodi-imides has not been developed. An exception is the direct silylation of isothiourea derivatives with a mixture of trimethylchlorosilane and triethylamine, which gives a 76% yield of bistrimethylsilylcarbodi-imide[91].

Isothiouronium salts can also be used as starting materials for the preparation of silylated carbodi-imide[91]:



There have been reports of the direct conversion of thiourea and its organic derivatives into organotin carbodi-imides[25,48], excess of the initial triphenyltin oxide being used as dehydrosulphurising agent:

$$Ph_3SnOSnPh_3 + H_2NCNH_2 \rightarrow Ph_3SnN{=}C{=}NSnPh_3 +$$
$$+ Ph_3SnSSnPh_3 + H_2O$$
$$Ph_3SnOSnPh_3 + Ph_3CNHCNH_2 \rightarrow$$
$$\rightarrow Ph_3SnN{=}C{=}NCPh_3 + Ph_3SnSSnPh_3 + H_2O .$$

This process is assumed to involve intermediate formation of triphenylstannylcyanamide, which disproportionates into the organotin carbodi-imide and dicyanodiamide (Eqns. 4b, 4c).[25] Replacement of triphenylmethylated thiourea by its phenyl analogue yields an organotin cyanamide instead of the expected carbodi-imide[30]:

$$Ph_3SnOSnPh_3 + PhNHCNH_2 \rightarrow Ph_3SnNC{\equiv}N + Ph_3SnSSnPh_3 + H_2O .$$

This result was attributed[30] to differences in the steric characteristics of the phenyl and triphenylmethyl groups.

Examples of the synthesis of silylcarbodi-imides from organosilicon ureas are very few[10,11,92]. Thus reaction of bistrimethylsilylurea with phenyl-lithium followed (after boiling) by trimethylchlorosilane gives an 80% yield of bistrimethylsilylcarbodi-imide[11]:

$$(Me_3SiNH)_2CO \xrightarrow[2)Me_3SiCl]{1)PhLi} Me_3SiN{=}C{=}NSiMe_3 .$$

Replacement of phenyl-lithium by sodamide lowered the yield to 12%.[11]

Use of the silver salt of imidazole to desulphurise bistrimethylsilylthiourea gave a 50% yield of bistrimethylsilylcarbodi-imide[12]:

$$Me_3SiNHC(S)NHSiMe_3 + AgC_3H_3N_2 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + Ag_2S + C_3H_4N_2 .$$

An organosilicon carbodi-imide containing an organic function has also been obtained from a thiourea derivative[91]:

$$Me_3SiOCH_2CH_2NHC(S)NHCH_2CH_2OSiMe_3 \xrightarrow{MeI} \rightarrow$$
$$\rightarrow [Me_3SiOCH_2CH_2NHC(SMe){=}NHCH_2CH_2OSiMe_3]^+ I^- \rightarrow$$
$$\xrightarrow{Me_3SiCl/Et_3N} [Me_3SiOCH_2CH_2N(SiMe_3)C(SMe){=}NCH_2CH_2OSiMe_3] \rightarrow$$
$$\xrightarrow{80^\circ} Me_3SiSMe + Me_3SiOCH_2CH_2N{=}C{=}NCH_2CH_2OSiMe_3 .$$

4. Reactions with Metallated Silylamines

This differs from the preceding methods in being applied exclusively to the preparation of organosilicon carbodi-imides. Reaction of the sodium and lithium derivatives of bistrimethylsilylamine $[(CH_3)_3Si]_2NM$ with carbonyl chloride[10,11,92], carbon dioxide[10,11,93-95], carbon disulphide[93,95], silicon-containing isocyanates and isothiocyanates[10,11,96-98], cyanogen halides[12,65,99], dithiocyanogen[100], trifluoroiodomethane[93], cyanuryl chloride[13], and isocyanide dichlorides [e.g. $C_6H_5.NCCl_2$][101,102] yields organosilicon carbodi-imides. Thus on phosgenisation of the sodium derivative in boiling benzene bistrimethylsilylcarbodi-imide was isolated in 60% yield[10,11,92]. It is of interest to note for comparison that the corresponding reaction with non-metallated silazane results in isolation of another heterocumulene–trimethylsilyl isocyanate[11]:

$$(Me_3Si)_2NH + COCl_2 \rightarrow Me_3SiN{=}C{=}O + Me_3SiCl + HCl .$$

The reaction of sodium bistrimethylsilylamine with carbon dioxide has a complicated course. The gas is rapidly absorbed by a benzene solution of the sodium derivative

even at room temperature to form bistrimethylsilylcarbodi-imide[93]. By analogy with the reactions of other hetero-organic compounds it would be expected that the alkali-metal silicon-containing carbamate or its decomposition products would be formed:

$$(Me_3Si)_2NNa + CO_2 \rightarrow (Me_3Si)_2NCOONa\ .$$

Nuclear magnetic resonance spectroscopy showed that actually the reaction involved a series of consecutive processes with initial formation of a salt of carbamic acid, which broke down into sodium trimethylsiloxide and trimethylsilyl isocyanate. When carbon dioxide was passed through molten sodium bistrimethylsilylamine at 200 °C the isocyanate could be isolated before it underwent further reactions[94]. The complete series of reactions can be represented by the overall equation[93]

$$(Me_3Si)_2NNa + CO_2 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2O + NaOCN + Na_2NCN + Na_2CO_3\ .$$

Carbon disulphide reacts similarly with sodium trimethylsilylamine[93]:

$$CS_2 + (Me_3Si)_2NNa \rightarrow NaSCN + Na_2S + (Me_3Si)_2S + Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_3N\ .$$

Reaction of sodium bistrimethylsilylamine with silicon tetra-isocyanate and with trimethylsilyl isocyanate and isothiocyanate results in all cases in the formation of bistrimethylsilylcarbodi-imide, but there is a difference in behaviour between isocyanato- and isothiocyanato-silanes: whereas the isothiocyanato-group in organosilicon isothiocyanates can act in these reactions as either a pseudohalogen or a thiocarbonyl group, isocyanates behave as typical carbonyl compounds without displaying any of the pseudohalogen properties so characteristic of most of their reactions. In particular, trimethylsilyl isocyanate undergoes solely the second possible type of reaction[98]:

$$Me_3SiNCO + (Me_3Si)_2NNa \rightarrow NaOCN + (Me_3Si)_3N$$
$$Me_3SiNCO + (Me_3Si)_2NNa \rightarrow (Me_3Si)_2O + Me_3SiN{=}C{=}NSiMe_3 + NaOCN\ .$$

Trimethylsilyl isothiocyanate reacts with the sodium derivative considerably less vigorously than does the isocyanate, the proportions of the parallel reactions being respectively 65–70% and 25%:[98]

$$Me_3SiNCS + (Me_3Si)_2NNa \rightarrow \begin{cases} Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2S + NaSCN \\ (Me_3Si)_3N + NaSCN\ . \end{cases}$$

The preparative value of this reaction is limited by the difficulty of separating the product mixture due to the only slight difference in boiling point between bistrimethylsilylcarbodi-imide and bistrimethylsilyl sulphide.

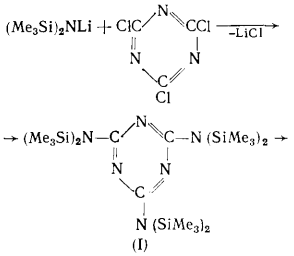
The action of sodium bistrimethylsilylamine on cyanogen halides[12,65,99], trifluoroiodomethane, and dithiocyanogen[93,100] gives high yields of bistrimethylsilylcarbodi-imide:

$$(Me_3Si)_2NNa + XCN \rightarrow Me_3SiN{=}C{=}NSiMe_3 + NaX \quad (X = Cl, Br, I)$$
$$(Me_3Si)_2NNa + ICF_3 \rightarrow NaI + NaF + Me_3SiF + Me_3SiN{=}C{=}NSiMe_3$$
$$(Me_3Si)_2NNa + (SCN)_2 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + NaSCN + (Me_3Si)_2NSSN(SiMe_3)_2\ .$$

As in the case of carbon dioxide, formation of the carbodi-imide in the last reaction is unexpected. It was assumed[100] to involve the series of reactions

$$(Me_3Si)_2NNa + NCS{-}SCN \rightarrow (Me_2Si)_2N{-}SCN + NaSCN$$
$$(Me_3Si)_2N{-}S{-}C{\equiv}N \rightarrow Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2NSS{-}CN$$
$$NC{-}S{-}\underset{\displaystyle SiMe_3}{\overset{\displaystyle |}{N}}{-}SiMe_3$$
$$(Me_3Si)_2N{-}S{-}SCN \rightarrow (Me_3Si)_2N{-}S{-}S{-}N(SiMe_3)_2 + (SCN)_2\ .$$

Reaction between lithium bistrimethylsilylamine and cyanuryl chloride in boiling oxolan gives a 25% yield of bistrimethylsilylcarbodi-imide[13] accompanied by 2,4,6-trishexamethyldisilazanyl-1,3,5-triazine, tristrimethylsilylamine, traces of hexamethyldisilazane, and an insoluble product of high melting point, which according to the infrared spectra is a lithium derivative of trimethylsilylcarbodi-imide. The reaction mechanism[13] involves initial formation of an organosilicon 1,3,5-triazine (I), its thermal decomposition, obviously to *NN*-bistrimethylsilylcyanamide, and rapid isomerisation of the latter to the carbodi-imide:



(I)

$$[(Me_3Si)_2NC{\equiv}N] \rightarrow Me_3SiN{=}C{=}NSiMe_3\ .$$

Heating pure (I) to 100 °C does actually give the carbodi-imide (85%). Formation of tristrimethylsilylamine and the lithium derivative $(CH_3)_3SiN:C:NLi$ was attributed[13] to partial interaction of lithium bistrimethylsilylamine with (I) or with bistrimethylsilylcarbodi-imide:

$$Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2NLi \rightarrow (Me_3Si)_3N + Me_3SiN{=}C{=}NLi\ .$$

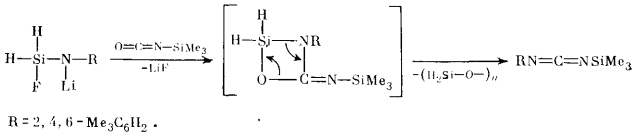
This process, like all the preceding methods, can be used to obtain unsymmetrical organosilicon carbodi-imides. Thus treatment of phenyl dichloroisocyanide with an equimolecular quantity of lithium bistrimethylsilylamine at 100 °C gives a 65% yield of *N*-phenyl-*N'*-trimethylsilylcarbodi-imide[101,102]:

$$PhN{=}C\begin{matrix}Cl\\Cl\end{matrix} + (Me_3Si)_2NLi \xrightarrow{LiCl} \left[PhN{=}C(Cl){-}N(SiMe_3){-}SiMe_3\right] \xrightarrow[-Me_3SiCl]{} PhN{=}C{=}NSiMe_3\ .$$

The same compound was obtained as a by-product from the reaction of phenyl isocyanate or isothiocyanate with methyldiphenyltrimethylsilyliminophosphorane $(C_6H_5)_2P(CH_3):NSi(CH_3)_3$.[103] *N*-t-Butyl-*N'*-trimethylsilylcarbodi-imide has been prepared from t-butyl isocyanate and lithium bistrimethylsilylamine[54]:

$$t\text{-}BuN{=}C{=}O + (Me_3Si)_2NLi \rightarrow t\text{-}BuN{=}C{=}NSiMe_3 + LiOSiMe_3\ .$$

An unsymmetrical organosilicon carbodi-imide has been obtained also by reaction between the lithium derivative of a fluorosilylamine and trimethylsilyl isocyanate[104]:



$R = 2,4,6\text{-}Me_3C_6H_2$.

Low yields of bistrimethylsilylcarbodi-imide result from the thermal decomposition of the nitrogen-containing lithium complexes[88]

$$(Me_3Si)_3N_2Li\cdot COS,\ (Me_3Si)_3N_2Li\cdot CS_2,$$
$$(Me_3Si)_2N_2Li_2\cdot COS,\ (Me_3Si)_2N_2Li_2\cdot CS_2,$$
$$(Me_3Si)_3N_2Li\cdot TsNCS\ .$$

5. Decarboxylation of Isocyanates

The decarboxylation of isocyanates is an important and most convenient method for obtaining organic carbodi-imides[1,3]. It is suitable also for preparing hetero-organic carbodi-imides, although very few papers have appeared on this topic. Thus, when trimethylsilyl isocyanate is passed through a quartz tube heated to ~600 °C, it undergoes partial decarboxylation to bistrimethylsilylcarbodi-imide[105,106]:

$$Me_3SiNCO \xrightarrow[-CO_2]{\Delta} Me_3SiN=C=NSiMe_3 .$$

At temperatures up to 200 °C this and other silyl isocyanates do not undergo the reaction even in the presence of decarboxylation catalysts[105,106]. In contrast, silicon-containing aromatic carbodi-imides

$$n\text{-}XC_6H_4N=C=NC_6H_4X\text{-}n \quad (X=HMe_2Si,\ Me_3Si,\ Me_3SiO)$$

have been obtained in 82–93% yields by heating the corresponding isocyanates in the presence of organo-phosphorus catalysts to 150–180 °C.[107,108].

The decarboxylation of organotin isocyanates is considerably more complicated. Thus triphenylstannyl isocyanate gives only a 19% yield of bistriphenylstannyl-carbodi-imide[109,110], which is attributed to the possibility of simultaneous disproportionation of the isocyanate to diphenylstannanediyl di-isocyanate and tetraphenyl-stannane[109–111]:

$$Ph_3SnN=C=O \begin{cases} \xrightarrow{-CO_2} Ph_3SnN=C=NSnPh_3 \\ \longrightarrow Ph_2Sn(NCO)_2 + Ph_4Sn \end{cases} .$$

Tributylstannyl isocyanate is extremely stable to heat, being only 4% decomposed when kept at 200 °C for 6 h; at 250 °C it breaks down into butane, butene, carbon monoxide, nitrogen, metallic tin, and an unidentified solid residue[109]. The course of the reactions is uninfluenced by the usual decarboxylation catalysts (water, hydroquinone, urea, etc.).[112] Tris(trimethylsilylmethyl)stannyl isocyanate is still more stable, breaking down at 275 °C after 6 h (yield 12%):[49]

$$(Me_3SiCH_2)_3SnNCO \rightarrow (Me_3SiCH_2)_3SnN=C=NSn(CH_2SiMe_3)_3 + CO_2 .$$

Triphenylplumbyl isocyanate is converted into the corresponding carbodi-imide $C[:NPb(C_6H_5)_3]_2$, but the yield is comparatively small[113]; the scheme of thermal decomposition has been subjected to detailed thermographic investigation[110].

Thus decarboxylation of isocyanates has at present limited value for the preparation of hetero-organic carbodi-imides.

6. Other Methods

Several papers have recently appeared on the formation of hetero-organic carbodi-imides and cyanamides by trans-metallation:

$$R_3MN=C=NMR_3 + 2R'_3M'X \rightarrow 2R_3MX + R'_3M'N=C=NM'R'_3$$

$M = M' = Si$; $R = Me$; $R' = Et$, Ph; $X = Cl$. $M = Si$; $M' = Ge$;
$R = Me$; $R'_3 = Me_nH_{3-n}$, $n = 0-3$; $X = F$. $M = Si$; $M' = Sn$;
$R = Me$; $R' = Ph$; $X = OH$. $M = Ge$; $M' = Si$; $R = R' = H$; $X = Br$.
$M = Ge$; $M' = Sn$; $R = Et$; $R' = Ph$; $X = Cl$; $M = Sn$. $M' = Si$;
$R = Bu$; $R' = Me$; $X = Cl$. (8)

Interaction of bistrimethylsilylcarbodi-imide with triphenyl-chlorosilane at 245–250 °C [14,15] gives a 75% yield of a new carbodi-imide. The action of fluorogermane on the former reactant at room temperature results in a 95% yield of digermylcarbodi-imide[14,114]. This method has been used also to obtain organogermanium carbodi-imides of general formula $C[:NGe(CH_3)_nH_{3-n}]_2$ (yields up to 90%).[16]

Digermylcarbodi-imide in turn reacts with bromosilane at room temperature to give a quantitative yield of germyl bromide and disilylcarbodi-imide[114]. Bistrimethylsilyl-carbodi-imide has been obtained from bistributylstannyl-carbodi-imide and trimethylsilyl chloride[115] or tristrimethyl-silyl cyanurate[61], bistriethylsilylcarbodi-imide from bistrimethylsilylcarbodi-imide and triethylsilyl chloride[66]. Bistriphenylstannylcarbodi-imide is formed as a by-product in the reaction of triphenyltin hydroxide with bistrimethyl-silyl- or bistriethylgermyl-carbodi-imide[116]. In the dehydration of *NN'*-bistrimethylsilylurea with excess of phenyltri-chlorosilane bisphenyldichlorosilylcarbodi-imide is formed as a result of parallel transsilylation[66]. The interaction of equimolecular quantities of bistributylstannylcarbodi-imide and trimethylchlorosilane revealed intermediate formation of *N*-tributylstannyl-*N'*-trimethylsilylcarbodi-imide[115], which like *N*-trimethylsilyl-*N'*-triphenylsilylcarbodi-imide dis-proportionated when an attempt was made to distil it[15].

Nuclear magnetic resonance proved also the possibility of obtaining unsymmetrical germylsilylcarbodi-imides by exchange processes[117]:

$$Me_2RSiN=C=NSiRMe_2 + Me_3GeN=C=NGeMe_3 \rightleftarrows$$
$$\rightleftarrows 2Me_2RSiN=C=NGeMe_3$$
$$R = H,\ Me .$$

Heating bistrimethylsilylcarbodi-imide with di- and tri-halogenosilanes and with halogenated alkylsiloxanes, while the trimethylchlorosilane evolved is distilled off, yields polymeric carbodi-imides of silicon as viscous oils or rubberlike substances of high thermal stability[118–121]. Organosilicon cyanamides can also undergo transmetallation: for example, triethylchlorosilane acts on *N*-allyl-*N*-tri-methylsilylcyanamide to give an 89% yield of *N*-allyl-*N*-triethylsilylcyanamide[66].

Hetero-organic cyanamides and unsymmetrical carbodi-imides can be obtained by the interaction of $C(:NMR_3)_2$ ($M = Si$, Sn; $R = Alk$, Ar) or $R_3SnNR'C:N$ ($R = Alk$, Ar; $R' = H$, Alk, Ar) with alkyl and aryl halides[5,112,122,123], acyl halides[4,5,124–129], and other compounds containing an active halogen atom[4,6,129–137] or a pseudohalogen group[30,66,137–139]. Carbodi-imides $(CH_3)_3SiN:C:NSO_2R$ ($R = F$, CF_3) have been obtained from bistrimethylsilylcarbodi-imide and the sulphonic anhydrides $(RSO_2)_2O$.[140] These reactions will be discussed in detail below.

The reaction of *N*-t-butyl-*N'*-trimethylsilylcarbodi-imide with dimethyldichlorosilane gives bis-t-butylcarbodi-imido-dimethylsilane[28]:

$$t\text{-}BuN=C=NSiMe_3 + Me_2SiCl_2 \rightarrow$$
$$\rightarrow Me_2Si\begin{matrix} N=C=NBu\text{-}t \\ N=C=NBu\text{-}t \end{matrix} + Me_3SiCl .$$

Bistrimethylsilylcarbodi-imide is formed above 120 °C from its isomer of unknown structure obtained by reaction of lithium diazomethane with trimethylchlorosilane and the arbitrarily named[141] bistrimethylsilylisodiazomethane. The structure $[(CH_3)_3Si]_2C:N^+:N^-$ was later[142,143] attributed to this last compound. Pure bistrimethylsilyldiazomethane proved to be highly thermostable, and did not rearrange into the carbodi-imide even when heated to 150 °C (in nonane for 7 days).[143] However, such rearrangement is catalysed by copper(II) sulphate and by products of secondary reactions formed in the preparation of the silylated diazomethane. Since products of the silylation of lithium diazomethane obtained by different investiga-tors[141–143] differed in properties, it was considered[144] that either a substituted diazomethane or bistrimethylsilyl aminoisocyanide $[(CH_3)_3Si]_2\ddot{N}.N^+:C:^-$ could be formed in this reaction depending on the conditions, and that either product when heated or in the presence of a catalyst isomerised into

bistrimethylsilylcarbodi-imide[144,145]. The aminoisocyanide was also obtained by an independent method[144]:

$$(Me_3Si)_2N{-}N{:}\ CCl_2 + BuLi \xrightarrow[-78^\circ]{Et_2O} \rightarrow (Me_3Si)_2\ddot{N}{-}\overset{+}{\ddot{N}}{\equiv}\overline{C}{:} + LiCl + BuCl\ .$$

Heating the product to 100 °C for 20 h did indeed give a 97% yield of bistrimethylsilylcarbodi-imide. This last compound is formed in 10–30% yields also when bistrimethylsilyl aminoisocyanide is heated with sulphur dioxide, trimethylsilylimine sulphoxide $(CH_3)_3SiN:S:O$, or bistrimethylsilylthiodi-imide $S[:NSi(CH_3)_3]_2$. The corresponding reaction with phenyl isocyanate yielded a mixture of trimethylsilyl isocyanate, *N*-phenyl-*N'*-trimethylsilylcarbodi-imide, and bistrimethylsilylcarbodi-imide in the proportions 1 : 1 : 0.3.[145]

Bistrimethylsilylcarbodi-imide has been obtained by the ultraviolet irradiation of pentacarbonyltrimethylsilylmanganese and acetonitrile at room temperature[146].

III. PHYSICOCHEMICAL PROPERTIES AND STRUCTURE

Carbodi-imides and cyanamides containing silicon, germanium, tin, and lead are colourless liquids or solids having a characteristic odour, fairly readily soluble in organic solvents. Hetero-organic carbodi-imides are considerably more stable, but the cyanamides are less stable, than the organic analogues: the hetero-organic carbodi-imides can be stored for many months almost without change[15], without the increase in viscosity due to polymerisation that is so characteristic of organic carbodi-imides. The hetero-organic compounds can usually be vacuum-distilled at 250 to 260 °C without decomposition. Bistriphenylsilylcarbodi-imide undergoes appreciable decomposition only above 266 °C.[15] Certain hydride and unsymmetrical carbodi-imides constitute exceptions[6,15,115,134], either breaking down or symmetrising even on slight heating.

Hetero-organic cyanamides $R_3MNR'C:N$ (M = Si, Sn; R = Alk, Ar; R' = H, Alk, Ar) are extremely unstable thermally, rapidly passing into the corresponding carbodi-imides when heated. With organotin compounds this reaction is irreversible[25,50], but with organosilicon compounds a tautomeric equilibrium is observed[4,40,41,67,68].

Polymeric organosilicon carbodi-imides $[SiRR'N:C:N]_n$ (R, R' = CH_3, C_6H_5, $CH_2:CH$) are colourless or pale brown, and are converted into viscous oils when heated above 100 °C. Their thermal stability is apparently determined by the presence of a certain number of siloxane units in the macromolecular chain[20], since some loss in weight is observed even at 200 °C. The infrared spectra remain almost unchanged even when specimens are heated in a vacuum to 350 °C for 2 h, an indication of the great thermal stability of the poly(silicon–carbodi-imide) grouping.

Bistributylstannyl-, bistriphenylstannyl-, and bistriphenylplumbyl-carbodi-imides are completely decomposed when heated above 250 °C.[109–112].

Measurements of the Trouton constant showed that both disilyl- and bistrimethylsilyl-carbodi-imides are weakly associated in the liquid phase[6,11]. Organotin cyanamides and certain carbodi-imides are far more strongly associated and can form dimers, trimers, or tetramers even in solvents[29,31,128,147]. The fact that the coordination number of tin exceeds 4 explains the ability of these compounds to form oligomers[5,25,29,31,126,128,147].

The carbodi-imide structure of the disilyl[148], bistriphenylsilyl[149], digermyl[150,151], and bistrimethylstannyl[5,18,19] compounds has been confirmed by X-ray or gaseous electron diffraction.

The heteroatom–nitrogen bond energies in hetero-organic carbodi-imides and the increment in molecular refraction have been found only for bistriethylstannylcarbodi-imide (respectively 103 ± 6 kcal mole^{-1} and 3.44 cm^3) [152] and bistributylstannylcarbodi-imide (100 ± 5 and 3.42).[47,153]

Most workers have used infrared spectroscopy to establish the structure of the hetero-organic cyanamides and carbodi-imides they have prepared. Much information has been obtained also from study of the Raman[7,8,16,65,68,154], n.m.r.[6,15,16,20,25,30,40,41,54,68,69,71,73,76,93,102,114,123,128,130,132–135,140,141,147,155–159], and mass[16,73,136] spectra. In some cases spectral and physicochemical characteristics of other hetero-organic heterocumulenes are given for comparison with data on carbodi-imides[9,11,65,82,112–114,136,137,150–152,155,160]. Infrared spectra establish quite unambiguously the appearance of a product of carbodi-imide structure in any reaction, from the characteristic frequency $\nu_{as}(N:C:N)$—respectively 2260–2170, 2160–2130, 2090–2070, and 2060 cm^{-1} for carbodi-imides containing silicon, germanium, tin, and lead.

Relative to the infrared spectra of analogous organic carbodi-imides [$\nu_{as}(N:C:N)$ 2150–2130 cm^{-1}] the organosilicon compounds exhibit a displacement of this band to higher frequencies, close to the C:N vibrations in organic cyanamides R_2NCN (2260–2210 cm^{-1}).[11,53] Nevertheless, the carbodi-imide structure—not the cyanamide structure—was adopted for the compounds $(R_3Si)_2N_2C$, on the grounds that their spectra contain neither the bands due to symmetrical N.C:N-stretching vibrations characteristic of cyanamides (~1200 cm^{-1}) [114] nor the unsymmetrical Si.N.Si vibrations at 934 cm^{-1} usually observed with other disilyl derivatives containing an Si_2N group[11]. Nor has the $\nu_s(N.C:N)$ band been found in the spectrum of digermylcarbodi-imide[114].

For the most thoroughly studied compounds—the bistrimethylsilyl, bistriethylstannyl, and bistributylstannyl derivatives—the carbodi-imide structure was adopted also in view of the comparatively small dipole moment, respectively 1.48 [12] (1.84 [161]), 1.79 ± 0.02, and 2.74 ± 0.02 D,[152] which compare with 4.5–4.8 D,[4,152,161] in the case of disubstituted organic cyanamides.

The carbodi-imide structure of the bisdimethylsilyl compound is supported convincingly also by ^{14}N n.m.r. spectral data: the spectrum contains only one signal, at 325 ppm (relative to ammonium nitrate).[15] It may be noted for comparison that dicyclohexylcarbodi-imide also gives only one resonance signal, at 240 ppm, whereas diethylcyanamide exhibits two clearly separated signals, at 149 and 258 ppm due to nitrilo- and amino-nitrogen atoms respectively[15]. The greater positive chemical shift displayed by bistrimethylsilyl- than by dicyclohexyl-carbodi-imide can be explained by the purely inductive effect of the silicon atom, which is more electropositive than carbon.

It is noteworthy that the $\nu_{as}(N:C:N)$ frequencies of organosilicon carbodi-imides containing an organic function (2160–2130 cm^{-1}) [91,107] lie in the same region as those of their carbon analogues.

The structures of hetero-organic cyanamides and unsymmetrical carbodi-imides of silicon[28,38–41,54,66–69,71,101,102,104,115,117,130–136,140,145,158,159], germanium[35,71,117,138], tin[25,27,29–37,50,73,115,123,125–129,137,139,162], and lead[29,51] have also been determined from infrared, Raman, n.m.r., mass, and Mössbauer spectral data together with X-ray diffraction results. In some cases, however, complete certainty has not yet been achieved that the choice between cyanamide and carbodi-imide forms is correct for individual compounds, since the physicochemical data sometimes do not provide unambiguous answers to such questions. Thus, whereas there is no doubt about the structure of *N*-triphenylmethyl-*N'*-triphenylstannylcarbodi-imide[25,30,123] (the corresponding

cyanamide form is improbable also as a consequence of great steric hindrance), the structure of the arenesulphonyl derivatives

$$R_3SnN{=}C{=}N{-}SO_2R' \qquad R_3SnN(SO_2R')-C{\equiv}N$$
(A) (B)

is debatable. On the basis of the infrared spectra (2193 cm^{-1}) the cyanamide structure (B: R = CH_3, C_6H_5; R′ = C_6H_5, p-$CH_3C_6H_4$, p-BrC_6H_4) has been attributed[30,126,128] to such compounds, since the ν(C:N) frequencies of organotin cyanamides of type $R_3SnNHC{:}N$ (R = CH_3, C_4H_9, C_6H_5) lie in the range 2183–2174 cm^{-1}.[25,50] On the other hand, there are good reasons for regarding such compounds as hetero-organic carbodi-imides by analogy with organic sulphonylcarbodi-imides [ν_{as}(N:C:N) 2180–2175 cm^{-1}].[163,164] Definite evidence in support of structure (A) is also the comparatively low dipole moment found for *N*-phenylsulphonyl-*N*′-tributylstannylcarbodi-imide (μ_{exp} = 5.4 ± 0.3 D, μ_{calc} = 5.04 D; for the cyanamide form μ_{calc} = 6.87 D).[129] The preparation has also been reported of *N*-phenylsulphonyl-*N*′-triethylgermylcarbodi-imide[138] and of $(CH_3)_3SiN{:}C{:}NSO_2R$ [R = F, CF_3, $(CH_3)_3SiO$],[136,140] whose carbodi-imide structure is not open to doubt; their ν_{as}(N:C:N) frequencies are respectively 2190 and 2250–2240 cm^{-1}.

Several investigations have been made recently on the structure of organosilicon cyanamides and unsymmetrical carbodi-imides[4,40,41,54,67–69]. The infrared spectra and the ^1H, ^{29}Si, and ^{13}C n.m.r. spectra have shown that the freshly prepared products of the reaction of secondary organosilicon amines with cyanogen chloride are carbodi-imides, which in time undergo a silatropic rearrangement and are converted into the corresponding cyanamides (Eqn.6). Heating again yields the original organosilicon carbodi-imides[40]. Formation of the cyanamide form is prevented by the steric effect of the t-butyl and phenyl groups.

Study of the reaction of cyanogen chloride with silylamides of carboxylic acids led to the conclusion that the products could exist in three tautomeric forms (A) ⇌ (B) ⇌ (C) (Eqn.7). The infrared spectra suggest that form (C) predominates[67,68]. In the case of the organotin analogues opinions on the structure of the products were divided. On the basis of infrared spectral data preference has been given[125,126,128] to form (B):

$$R'C(=O)N{=}C{=}NSnR_3 \rightleftarrows R'C(=O)N(SnR_3)-C{\equiv}N \rightleftarrows R'-C(OSnR_3){=}N-C{\equiv}N$$
(A) (B) (C)

R = Me, Ph; R′ = Me, Et, CF_3, $PhCH_2$, p-$O_2NC_6H_4$, p-FC_6H_4, p-ClC_6H_4, MeO, EtO.

Other workers have shown[127,162] that tautomers can be formed with compounds of this type having R = C_4H_9 and R′ = C_6H_5, but structure (C) is thermodynamically the most stable. The position of equilibrium in such systems is displaced under the influence of heating and additions of tributyltin chloride. Other discussions of the structures of such products have appeared[31,73].

The nitrile band in the infrared absorption spectra of organosilicon cyanamides containing an organic function $CH_3SiRR'CH_2NR''C{:}N$ (R = CH_3, C_2H_5O; R′ = CH_3O, C_2H_5O; R″ = iso-C_3H_7, iso-C_4H_9, C_6H_5)[53] lies in the range 2228 to 2211 cm^{-1}. Polymeric carbodi-imides $[SiRR'NCN]_n$ [n = 6–8; RR′ = $(CH_3)_2$, $(C_6H_5)_2$, $CH_3.C_6H_5$, $CH_3.CH_2{:}CH$, $(C_2H_5O)_2$] contain a strong N:C:N band at 2200–2150 cm^{-1}. The position of ν_{as}(N:C:N) is little affected by different substituents attached to the silicon atom. In the spectrum of the organotin tetramer $[(C_4H_9)_2SnN{:}C{:}N]_4$ this band has its maximum at 2063 cm^{-1}.

Study of n.m.r. spectra showed that the resonance signal of protons in organic groups attached to a silicon atom shifts upfield on passing from chlorosilanes to monomeric or polymeric organosilicon carbodi-imides. This indicates that the carbodi-imide group is less electronegative than the chlorine atom[15,20]. Thus for bistrimethylsilylcarbodi-imide and trimethylchlorosilane the difference is $\Delta\delta$ = 0.425 – 0.157 = 0.268 ppm.[20] This difference is increased when more than one chlorine atom is replaced by carbodi-imido-groups[20].

IV. CHEMICAL PROPERTIES

Hetero-organic carbodi-imides have very unusual chemical properties: in contrast to their organic analogues they can react not only at the carbodi-imide group but also at the heteroatom–nitrogen bonds. Furthermore, interaction between the N=C=N and M–N fragments results in a redistribution of electron density in the M–N=C=N system, with a consequent substantial change in reactivity of the compound as a whole. Thus the reactions of hetero-organic carbodi-imides can be divided into two main groups—(A) those accompanied by fission of heteroatom–nitrogen bonds and (B) additions at the cumulative double bonds.

The chemical properties of hetero-organic cyanamides will be considered at the same time and compared with those of the carbodi-imides.

A. Reactions with Fission of Heteroatom–Nitrogen Bonds

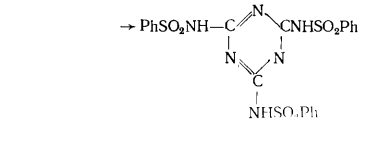
1. Interaction with compounds having a mobile hydrogen atom

Reactions of type (A) include primarily those of hetero-organic carbodi-imides with compounds containing a mobile hydrogen atom, e.g. water, alcohols, carboxylic acids. In contrast to organic carbodi-imides, which tend to undergo additions as a consequence of the unsaturation of the carbodi-imide group[1,3], their hetero-organic analogues are characterised by substitutions.

Hetero-organic carbodi-imides are usually quite stable towards atmospheric moisture under normal conditions. Thus bistriphenylsilylcarbodi-imide remains unchanged on contact with water for 10 days.[15] The enhanced hydrolytic stability of this class of compounds is explained by strengthening of heteroatom–nitrogen bonds due to delocalisation of electron density throughout the heterocumulene system under the influence of Group IVB elements[104,165,166]. However, prolonged heating of hetero-organic carbodi-imides with water results in fission of heteroatom–nitrogen bonds and separation of the coresponding hetero-organic oxides or hydroxides, together with cyanamide or a derivative thereof. Data have been published[11,25,28,44] on the hydrolysis of carbodi-imides containing silicon, germanium, and tin.

The hydrolysis of *N*-difluorophosphoryl-*N*′-trimethylsilylcarbodi-imide yields not only hexamethyldisiloxane and cyanamide but also phosphoric acid and hydrogen fluoride[132]. *N*-Phenylsulphonyl-*N*′-tributylstannylcarbodi-imide with water undergoes the reaction[129]

$$Bu_3SnN{=}C{=}NSO_2Ph \xrightarrow[-Bu_3SnOH]{H_2O} [PhSO_2NHCN] \rightarrow$$



Under similar conditions *N*-trimethylphenyl-*N'*-triphenylstannyl- and bistriphenylplumbyl-carbodi-imides do not react with water[25,49].

Hydrolysis of bistriethylgermyl- and bistriphenylgermylcarbodi-imides proceeds farther on the addition of 5–10% of sodium hydroxide to the reaction system. The final products are in the former case urea, cyanates, and hexaethyldigermoxane[45], and in the latter case urea, a mixture of cyanates, and sodium triphenylgermyl oxide[44].

Germanium-containing carbodi-imides react with water and hydrogen chalcogenides (sulphide, selenide, telluride) at room temperature[16,24]:

$$Me_nH_{3-n}GeN{=}C{=}NGeH_{3-n}Me_n + H_2El \rightarrow (Me_nH_{3-n}Ge)_2El + (H_2NCN)_2$$
$$El = O, S, Se;\ n = 0{-}3\ .$$

Similarly, bistriphenylplumbylcarbodi-imide is quantitatively converted by hydrogen sulphide at room temperature into bistriphenylplumbyl sulphide $S[Pb(C_6H_5)_3]_2$ and cyanamide[49]. Bistrimethylsilylcarbodi-imide, in contrast to the germanium and lead analogues, does not react with the hydrogen chalcogenides even when heated to 60–100 °C.[11-16]

Carbodi-imides containing silicon[16,116,117,168,169], germanium[114,116,117,168,169], and tin[25,55] react with alcohols and carboxylic acids to give the corresponding alkoxy- or acyloxy-derivatives together with cyanamide, dicyanodiamide, or melamine. Reaction takes place over a wide temperature range depending on the type and nature of the initial compounds. Thus digermylcarbodi-imide reacts rapidly and quantitatively with methanol at room temperature[114], whereas bistrimethylsilylcarbodi-imide requires heating to 100 °C.[116] The reaction of bistributylstannylcarbodi-imide with alcohols is reversible[55].

N-Triphenylmethyl-*N'*-triphenylstannylcarbodi-imide is decomposed by acetic acid under mild conditions to give triphenylstannyl acetate and triphenylmethylcyanamide[25].

In contrast to the above results, bistriphenylplumbylcarbodi-imide and trimethylplumbylcyanamide do not react with alcohols, and can be prepared in ethanol[49,51].

The reactions of bistrimethylsilyl- and bistriethylgermylcarbodi-imides[116] with hydroxylated compounds such as triethylsilanol and triphenyltin hydroxide also involve fission of heteroatom–nitrogen bonds, but they are complicated by simultaneous reaction between the initial carbodi-imides and water liberated on dehydration of the hydroxides:

$$R_3MN{=}C{=}NMR_3 + Ph_3SnOH \rightarrow Ph_3SnN{=}C{=}NSnPh_3 + R_3MOH$$
$$R_3MOH \xrightarrow{-H_2O} R_3MOMR_3\ .$$

The reaction of carbodi-imides containing Group IVB elements with thiols[16,117] and selenols[117,165,166,170] have a similar course to those with alcohols and lead to the separation of dicyanodiamide and the corresponding hetero-organic sulphur or selenium derivatives:

$$R_3MN{=}C{=}NMR_3 + REIH \rightarrow R_3MEIR' + (H_2NCN)_2$$
$$EL = S:\ M{=}Ge;\ R_3 = H_3,\ H_2Me,\ HMe_2,\ Me_3;$$
$$R'{=}Me,\ Et,\ Bu,\ Ph,\ Ac;\ El = Se:\ M = Si;$$
$$R{=}Me;\ R'{=}Bu;\ M{=}Ge;\ R{=}H,\ Et,\ Ph;$$
$$R'{=}Me,\ Bu,\ Ph;\ M{=}Sn;\ R{=}R'{=}Bu\ .$$

Bistrimethylsilylcarbodi-imide either does not react at all with thiols or gives insignificant [sic] 39–40% yields[16]. The SiN : C : NSi heterocumulene system is less liable to nucleophilic attack by heavy chalcogenols RSH, RSeH, and RTeH than is the corresponding GeN : C : NGe system. This is attributed to the enhanced stability of the silicon–nitrogen bond in carbodi-imides resulting from d_π–p_π interaction between the silicon and nitrogen atoms. The possibility of rupture of this bond by alcohols and acids is due to formation of the energetically more favourable silicon–oxygen bond[16]. The quantitative formation of products on treatment of germanium-containing carbodi-imides with these reagents results from the less double-bonded character of the germanium and nitrogen atoms.

The action of thioacetic acid on $C(:NSiR_3)_2$ ($R = H, CH_3$) and $C(:NGeR_3)_2$ [$R_3 = H_3, H_2CH_3, H(CH_3)_2, (CH_3)_3$] yields the corresponding thioacetates[168]. Spectral data show that in organosilicon thioacetates $R_3Si.O.CS.CH_3$ the R_3Si group is attached to the oxygen atom, whereas in the corresponding organogermanium derivatives $R_3Ge.S.CO.CH_3$ the R_3Ge group is attached to the sulphur atom.

Bistrimethylsilyl- and bistrimethylgermyl-carbodi-imides react vigorously with nitric acid at 0 °C to give the hetero-organic nitrates[171]:

$$Me_3MN{=}C{=}NMMe_3 + HNO_3 \rightarrow Me_3MONO_2 + (H_2NCN)_2\ .$$

Bistrimethylgermylcarbodi-imide reacts[117] with diphenylphosphine and phenylacetylene. The compounds $C[:NM.(CH_3)_3]_2$ (M = Si, Ge) do not react with phosphine, arsine, dimethylarsine, triphenylsilane, trimethylsilane, or pyrrole.

Bistrimethylsilylcarbodi-imide is reduced by lithium tetrahydroaluminate[15]:

$$Me_3SiN{=}C{=}NSiMe_3 + LiAlH_4 \rightarrow Me_3SiH + Li_2NCN + Al_2(NCN)_3\ .$$

Bistriphenylstannylcarbodi-imide is split by cyanamide[25]:

$$Ph_3SnN{=}C{=}NSnPh_3 + H_2NCN \rightarrow Ph_3SnNHCN\ .$$

Organosilicon carbodi-imides differ from their organic analogues in not reacting with ammonia or aniline, not adding hydrogen even in the presence of a palladium catalyst, and not causing amino-acids to condense to peptides[11].

2. Reactions with halogens and halogen-containing compounds

The action of halogens and their compounds on carbodi-imides containing silicon, germanium, and tin also involves fission of the heteroatom–nitrogen bond with formation of the corresponding hetero-organic halides and of cyanamide derivatives. Among halogen-containing compounds used have been hydrogen, alkyl, aryl, and acyl halides and Lewis acids. Only one publication[45] has described the reaction with an elementary halogen: bistriethylgermylcarbodi-imide reacts with bromine in benzene at 20 °C to give up to 70% yields of triethylgermyl bromide accompanied by dicyanodiamide and a polymer of undetermined structure. Disilylcarbodi-imide reacts with hydrogen chloride[6] to form chlorosilane and a compound to which the formula $H_2NCCl_2NH_2$ was assigned. A little later a similar reaction was accomplished with bistrimethylsilylcarbodi-imide, for which the scheme

$$R_3SiN{=}C{=}NSiR_3 + HCl \rightarrow R_3SiCl + Cl^- [H_2\overset{+}{N}{=}C{=}\overset{+}{N}H_2]\ Cl^-$$

was suggested[11].

Unsymmetrical *N*-trifluorosilyl-*N'*-trimethylsilylcarbodi-imide on treatment with excess of hydrogen chloride gives a quantitative yield of trimethylchlorosilane, chlorotrifluorosilane, and cyanamide dihydrochloride[130]:

$$Me_3SiN{=}C{=}NSiF_3 + HCl \rightarrow Me_3SiCl + F_3SiCl + H_2NCN{\cdot}2HCl\ .$$

When dry hydrogen chloride is passed through bistributylstannylcarbodi-imide at room temperature for 2 h the dihydrochloride is accompanied by tributyltin chloride (94%).[122]

Hetero-organic carbodi-imides react with metal salts of the Lewis acid type. Thus the reaction of disilylcarbodi-imide with silver chloride, bromide, and thiocyanate (at −78 °C for 18 h) gave low yields of chlorosilane, bromosilane, and isothiocyanatosilane respectively[6]. Treatment of bistriethylstannylcarbodi-imide with metal chlorides in boiling moist ether yields hydrates of the metal salts of cyanamide[5,167]:

$$Et_3SnN{=}C{=}NSnEt_3 + MCl_2 \rightarrow Et_3SnCl + MNCN\cdot nH_2O$$
$$M = Cu,\ Zn,\ Cd,\ Ca,\ Sn\ .$$

Products of the reaction with copper(II) sulphate are the monohydrate of copper(II) cyanamide $CuNCN.H_2O$ (91%) and bistriethylstannyl sulphate (98%).[167]

Hetero-organic carbodi-imides and cyanamides react very peculiarly with alkyl and aryl halides[5,112,122,123] and with arenesulphonyl chlorides[125,126,128,129,137,172]. Thus with ethyl and pentyl bromides bistributylstannylcarbodi-imide gives high yields of tributylstannyl bromide and the dialkylcyanamide[5,112,122]:

$$Bu_3SnN{=}C{=}NSnBu_3 + RBr \xrightarrow[84}{110-120^\circ} \rightarrow$$
$$\rightarrow Bu_3SnBr + \left[\begin{array}{c} Bu_3Sn \\ \diagdown \\ R \end{array}\!\!>\!N{-}C{\equiv}N\right] \xrightarrow{RBr} R_2NCN + Bu_3SnBr\ .$$

Bistriphenylstannylcarbodi-imide, in contrast to its butyl analogue, does not react with ethyl bromide (when boiled in acetonitrile), but with ethyl iodide triphenylstannyl iodide has been isolated[123]. With benzyl bromide it gives as final products triphenylstannyl bromide and the dibenzylcyanamide complex of the latter $(C_6H_5CH_2)_2NCN.(C_6H_5)_3SnBr$. An analogous reaction with *N*-triphenylmethyl-*N'*-triphenylstannylcarbodi-imide leads to isolation of the corresponding complex $(C_6H_5)_3C(C_6H_5CH_2)NCN.(C_6H_5)_3SnBr$.[123] Replacement of benzyl bromide by triphenylmethyl chloride yields either bistriphenylmethyl- or *N*-triphenylmethyl-*N'*-triphenylstannyl-carbodi-imide depending on the initial ratio of the reactants:

$$Ph_3SnN{=}C{=}NSnPh_3 \begin{cases} \xrightarrow[-Ph_3SnCl]{Ph_3CCl} Ph_3SnN{=}C{=}NCPh_3 \\ \xrightarrow[-2Ph_3SnCl]{2Ph_3CCl} Ph_3CN{=}C{=}NCPh_3 \end{cases}\ .$$

Here the usual exchange process is observed: the mechanism with migration of the reaction centre is not realised owing to the large bulk of the triphenylmethyl group[123].

Reaction of triphenylstannylcyanamide with triphenylmethyl chloride in the presence of triethylamine in the proportions 1 : 1 : 2 in benzene at 20 °C yields triethylamine hydrochloride (56%), bistriphenylmethylcarbodi-imide (38%), and *N*-triphenylmethyl-*N'*-triphenylstannylcarbodi-imide (5%).[123]

Organotin carbodi-imides and cyanamides react also with arenesulphonyl halides and pseudohalides. Thus the action of benzenesulphonyl chloride on bistributylstannylcarbodi-imide yields *N*-phenylsulphonyl-*N'*-tributylstannylcarbodi-imide and tributylstannyl chloride independently of the initial proportions of the reactants[129,137,172]; benzenesulphonyl azide reacts similarly[137,172]:

$$Bu_2SnN{=}C{=}NSnBu_3 + PhSO_2X \rightarrow Bu_3SnX + Bu_3SnN{=}C{=}NSO_2Ph$$
$$X = Cl,\ N_3\ .$$

Other publications have appeared[126,128] on the interaction of organotin carbodi-imides and arenesulphonyl chlorides, but a cyanamide structure was attributed to the products, as already mentioned:

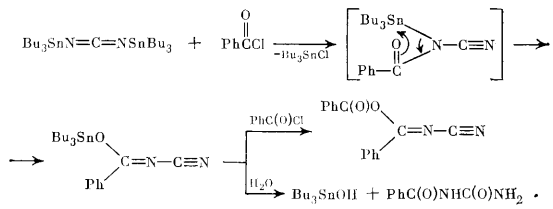
$$R_3SnN{=}C{=}NSnR_3 + R'Cl \rightarrow \underset{|}{\overset{C{\equiv}N}{R'NSnR_3}} + R_3SnCl \qquad (9)$$
$$R = Me,\ Ph;\ R' = PhSO_2,\ p\text{-}MeC_6H_4SO_2,\ p\text{-}BrC_6H_4SO_2\ .$$

In contrast to carbodi-imides triphenylstannylcyanamide forms with benzenesulphonyl chloride in the presence of triethylamine an anionic complex[125]:

$$Ph_3SnNHC{\equiv}N + RCl + Et_3N \rightarrow [RN(CN)SnPh_3Cl]^-[Et_3NH]^+ \qquad (10)$$
$$R = Ph,\ SO_2\ .$$

Reactions with acyl halides[4,5,124-129] also correspond to Eqns.(9) and (10),[125,126,128] but yield more complicated product mixtures, owing to the possibility of heterotropic rearrangements of the cyanamides (or carbodi-imides) formed. Bistrimethyl-, bistributyl-, and bistriphenylstannylcarbodi-imides react with acid chlorides at room temperature in the absence of a solvent[127,129] or in oxolan[125,126,128] to give the corresponding stannyl chlorides and cyanamide derivatives [Eqn.(9): R = CH_3, C_4H_9, C_6H_5; R' = CH_3CO, C_6H_5CO, $C_6H_5CH_2CO$, *p*-$CH_3C_6H_4CO$, *p*-$NO_2.C_6H_4CO$, *p*-ClC_6H_4CO, *p*-BrC_6H_4CO, CH_3OCO, CF_3CO]. The structure of these and the products of the reaction of bistrimethylsilylcarbodi-imide with trifluoroacetyl chloride[124] and with benzoyl chloride[4,66-68] has been discussed already (Sections II, 2 and III).

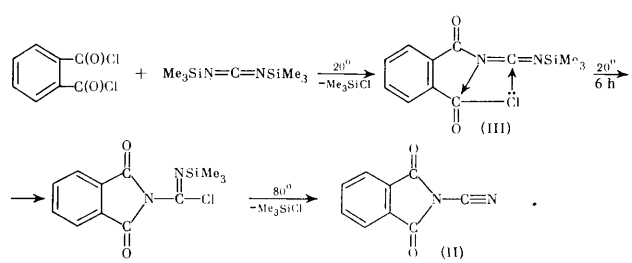
It is noteworthy that benzoyl chloride is able to react with bistributylstannylcarbodi-imide also in the proportions 2 : 1,[129] a process that is shown by the infrared spectra to take place in stages. One of the tin-nitrogen bonds is broken at room temperature within a few minutes, with formation of a substituted cyanoimine; reaction with the second molecule of benzoyl chloride takes place at 100 °C:



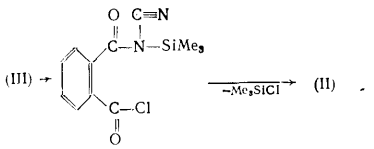
Hydrolysis of the intermediate organotin cyanamide leads to formation of benzoylurea[129].

Triphenylstannylcyanamide reacts with acid chlorides in conformity with Eqn.[(10): R = CH_3CO, C_2H_5CO, C_6H_5CO, CH_3OCO, C_2H_5OCO, $C_6H_5CH_2OCO$]. The corresponding anionic complexes were isolated as final products[125,126]. One such complex (R = CH_3CO) was obtained by cross synthesis from *N*-cyano-*N*-triphenylstannylacetamide and triethylamine hydrochloride[125]. Anionic complexes of the type $[N{:}C.N{:}C(NHR).OSn(C_6H_5)_3Cl]^-[(C_2H_5)_3NH]^+$ (R = C_2H_5, C_6H_5) have been prepared similarly[173].

The reaction of bistrimethylsilylcarbodi-imide with phthaloyl dichloride led to the isolation only of the final acylation product (II), whose formation was assumed[174] to involve the processes:



Alternatively, the reaction might involve intermediate formation of a cyanamide derivative:



The action of terephthaloyl and *p*-nitrobenzoyl chlorides on triphenylstannylcyanamide and triethylamine yields not complexes but triethylammonium salts of the corresponding acylcyanamides[125].

Organosilicon carbodi-imides are often used as intermediates in the preparation of novel hetero-organic compounds. The reaction of disilylcarbodi-imide with boron trifluoride was described as early as 1962:[7] an addition product is formed at −78 °C, which at room temperature breaks down into fluorosilane and *N*-boryl-*N*-silylcyanamide. The action of boron trifluoride on bistrimethylsilylcarbodi-imide yields trimethylfluorosilane and an unidentified polymer[117].

This communication served to initiate a large number of studies on the preparation of unsymmetrical organosilicon carbodi-imides and hetero-organic cyanoimines. Thus treatment of bistrimethylsilylcarbodi-imide with silicon tetrafluoride[130,131], phosphoryl trifluoride[132,133], thiophosphoryl trifluoride[134], $S:PF_2.N:PF_3$,[135] and $(CH_3)_3SiO_3.SCl$ [136] has yielded the corresponding halogenosilanes and carbodi-imides:

$$Me_3SiN{=}C{=}NSiMe_3 + RX \rightarrow Me_3SiN{=}C{=}NR + Me_3SiX$$
$$R = SiF_3,\ POF_2,\ PSF_2,\ S{=}PF_2N{=}PF_2;\ X = F;$$
$$R = SO_3SiMe_3;\ X = Cl\ .$$

Treatment with sulphur tetrafluoride[175,176], thionyl tetrafluoride[177,178], R_2NSF_3,[179,180] R_2NSOF_3 ($R = CH_3$, C_2H_5, C_5H_{10}),[179,181] $C_6H_5OSOF_3$,[182] $(CF_3)_2CFSF_3$,[183] $C_6H_5PF_4$, $(C_6H_5)_2PF_3$,[133,184,185] and thionyl dichloride[74-76] involves detachment of both trimethylsilyl groups to give up to 65% yields of cyanoimines:

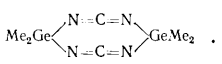
$$Me_3SiN{=}C{=}NSiMe_3 + YX_2 \rightarrow Y{=}N{-}C{=}N + Me_3SiX$$
$$Y = F_2S,\ F_2SO,\ Alk_2NS(O)F;\ (CF_3)_2CFSF,\ PhPF_2,$$
$$Ph_2PF;\ X = F;\ R = SO;\ X{=}Cl\ .$$

Depending on the conditions treatment with sulphur tetrafluoride may yield products differing in structure[176]:

$$F_2S{=}N{-}C{\equiv}N \xleftarrow[50°]{SF_4} Me_3SiN{=}C{=}NSiMe_3 \xrightarrow[200°]{SF_4} F_2S{=}NSF_2N{=}SF_2\ .$$

Exchange reactions between silylcarbodi-imides and inorganic halides were partly covered in a review[186].

The reported[117] reaction of bistrimethylsilylcarbodi-imide with germanium tetrafluoride and dimethylgermanium difluoride gave as final products not only trimethylfluorosilane but also a polymer containing fluorine, germanium, and nitrogen together with the compounds bisdimethylfluorogermylcarbodi-imide and



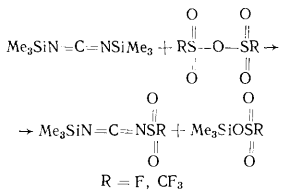
The transmetallation of hetero-organic carbodi-imides by means of organo-silicon, -germanium, and -tin halides has already been discussed in detail (Eqn.8).[1,4,14-16,66,114,115,117-121]

The reactions of unsymmetrical organosilicon carbodi-imides with hydrogen-containing compounds do not differ fundamentally from those of their symmetrical analogues. Thus the action of dimethyldichlorosilane and also of chlorine-containing sulphur compounds (sulphur dichloride and R_2NSCl) on *N*-t-butyl-*N'*-trimethylsilylcarbodi-imide has been described[158]. Elimination of trimethylchlorosilane led to isolation of the corresponding carbodi-imides:

$$t\text{-}BuN{=}C{=}NSNR_2 (R = Me,\ Et),$$
$$t\text{-}BuN{=}C{=}NSiMe_2N{=}C{=}NBu\text{-}t,$$
$$t\text{-}BuN{=}C{=}NSN{=}C{=}NBu\text{-}t\ .$$

3. Reactions with compounds containing S–O–S and P–O–P links

Bistrimethylsilylcarbodi-imide undergoes exchange processes also with compounds containing labile S–O–S and P–O–P bonds. Thus with disulphuryl difluoride and bistrifluoromethide at room temperature the corresponding unsymmetrical organosilicon carbodi-imides are obtained[140]:

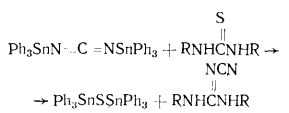


The reaction with pyrophosphoryl tetrafluoride $O(POF_2)_2$ apparently follows the same course[187], to give $(CH_3)_3.SiOPOF_2$ (85%) and an unidentified colourless solid.

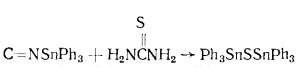
4. Interaction with thiourea derivatives and thioamides

The action of substituted thioureas and thioamides on organotin carbodi-imides and cyanamides also involves reactions of type (A).

When disubstituted thioureas are heated with bistriphenylstannylcarbodi-imides in boiling acetonitrile for 20 h, 45–74% yields of the corresponding *NN'*-disubstituted *N''*-cyanoguanidines and bistriphenylstannyl sulphide are obtained[25]:

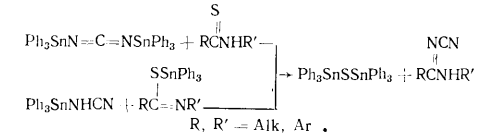


However, the use of thiourea results in the formation of triphenylstannylcyanamide, which can be explained by the scheme[25]:



Reaction of trimethyl- and triphenyl-stannylcyanamides with various isothioureas makes it possible to obtain the corresponding *N*-cyano-*S*-trialkylstannylisothioureas of general formula $R'N:C(NHCN)SSnR_3$ ($R = CH_3$, C_6H_5; $R' = CH_3$, C_6H_5, $p\text{-}FC_6H_4$, $p\text{-}NO_2C_6H_4$, $C_6H_5CH_2$, cyclo-C_6H_{11}).[188]

The reactions of bistriphenylstannylcarbodi-imide and of triphenylstannylcyanamide with *N*-substituted thioamides at room temperature in acetonitrile (63 h) or in ethanol (15 h) resulted in the same products—the corresponding *N'*-substituted cyanamidines (yields 25–67%):[189]



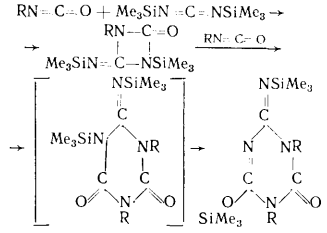
Treatment of the above carbodi-imides with thioamides in

ether or acetonitrile led to the isolation of acetonitrile or benzonitrile, bistriphenylstannyl sulphide, and dicyanodiamide. The sulphide and the organic nitrile could have been formed by decomposition of an intermediate compound of the type $(C_6H_5)_3Sn.S.CR:N.Sn(C_6H_5)_3$.[189]

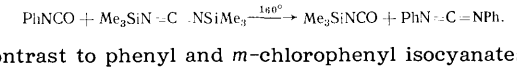
Several reactions of tin-containing carbodi-imides and cyanamides have been systematised in annual reviews on organotin compounds[190,191].

B. Additions at Cumulative Bonds of Carbodi-imides

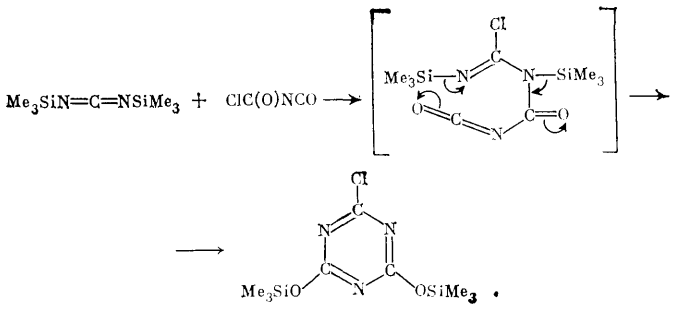
As mentioned above, addition reactions are far less characteristic of hetero-organic carbodi-imides than of the organic analogues. The first mention of reactions of this type related to that between bistrimethylsilylcarbodi-imide and fluorosulphuryl isocyanate $FSO_2N:C:O$.[192] An equimolecular adduct was formed, whose pyrolysis yielded trimethylfluorosilane. The carbodi-imide reacts with benzenesulphonyl isocyanate when heated to 100–150 °C,[138] with the formation of four- or six-membered heterocycles containing silicon depending on the initial proportions of the reactants:



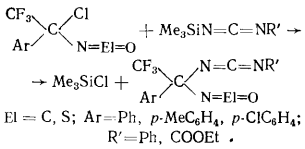
Such a scheme was suggested for the interaction of organic isocyanates with organic carbodi-imides[164,193]. In the case of phenyl isocyanate the only product of the reaction is the 1:2 adduct 2-oxo-1,3-diphenyl-4-trimethylsiloxy-6-trimethylsilylimino-1,2,3,6-tetrahydro-1,3,5-triazine (yield 82%).[194,195] A similar reaction occurs with *m*-chlorophenyl isocyanate[196]. If the low-boiling trimethylsilyl isocyanate formed is distilled off, an exchange reaction occurs with phenyl isocyanate[66]:



In contrast to phenyl and *m*-chlorophenyl isocyanates, chloroformyl isocyanate reacts with bistrimethylsilylcarbodi-imide in equimolecular proportions under mild conditions (in ether at 20 °C) to give a 64% yield of 2-chloro-4,6-bistrimethylsiloxy-1,3,5-triazine[197]:

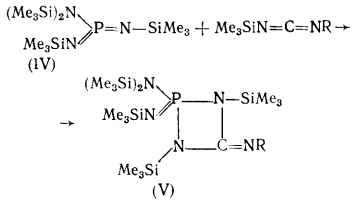


The reaction is seen to begin with electrophilic addition of the isocyanate at the carbon–nitrogen double bonds of the carbodi-imide. The product cyclises with simultaneous migration of the trimethylsilyl groups from nitrogen to oxygen atoms. Unsymmetrical organosilicon carbodi-imides undergo exchange reactions with chlorinated isocyanates; as final products have been isolated for the first time compounds having two different heterocumulene groups attached to the same carbon atom[38,39,198]:

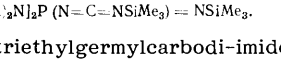


El = C, S; Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4; R′ = Ph, COOEt .

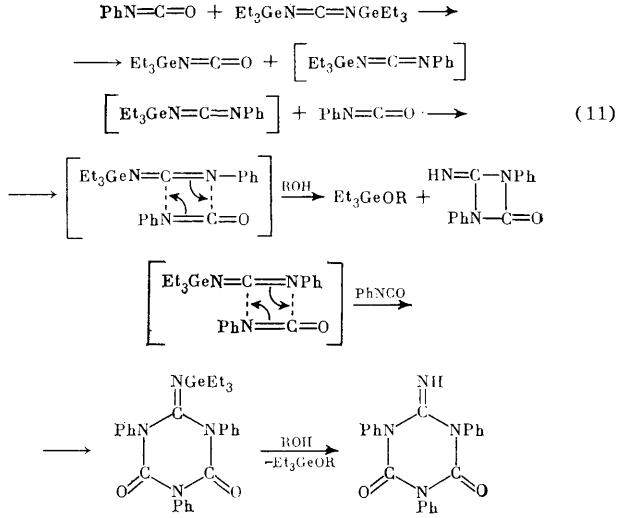
Interaction of bistrimethylsilyl- or *N*-t-butyl-*N*′-trimethylsilyl-carbodi-imide with the fully *N*-trimethylsilylated aminodiiminophosphorane (IV) at 0 °C for 2 h yielded cyclic adducts:



[R = $(CH_3)_2Si$, $(CH_3)_3C$].[159] When the reaction conditions were changed to 25 °C for 7 days, the product was not the compound [V: R = $(CH_3)_3Si$] but the carbodi-imidophosphinoimine:



The reaction of bistriethylgermylcarbodi-imide with phenyl isocyanate in the proportions 1:2 follows a rather different course[194]. Initial exchange of one of the triethylgermyl groups for phenyl is followed by cycloaddition of the resulting unsymmetrical carbodi-imide to a second phenyl isocyanate molecule; at the same time an organogermanium 1,3,5-triazine is formed to a slight extent:



(11)

R = H, Me, Et, iso-Pr .

Hydrolysis of the resulting organogermanium cycloadducts yields the corresponding organic isoammelide derivatives, as in the case of the organosilicon analogues. The action of benzenesulphonyl isocyanate involves mainly the first stage of reaction (11), which on heating is complicated by considerable resinification[138]. The final products isolated were triethylgermyl isocyanate (yield 34%) and *N*-phenylsulphonyl-*N*′-triethylgermylcarbodi-imide.

Benzenesulphonyl isocyanate reacts in just the same way when heated with bistributylstannylcarbodi-imide, giving an 83% yield of tributylstannyl isocyanate[138]. At 25 °C this carbodi-imide forms with benzenesulphonyl, phenyl, and 6-chlorohexyl isocyanates linear adducts of length depending on the initial proportions of the reactants[59,138,199,200]. Heating the adduct $C[:NSn(C_4H_9)_3]_2.3C_6H_5NCO$ and then hydrolysing the resulting mixture yielded several products indicating a reaction mechanism similar to (11). In particular 2-imino-4,6-dioxo-1,3,5-triphenylperhydro-1,3,5-triazine and triphenyl isocyanurate were isolated in yields of 61% and 30% respectively. Formation of the latter compound is apparently due to catalytic cyclotrimerisation of phenyl isocyanate under the influence of organotin compounds, which has been studied thoroughly[201,202]. Thermal decomposition of the adduct $C[:NSn(C_4H_9)_3]_2.ClC_6H_{12}NCO$ (at 200 °C for 4–5 h) gives tributyltin chloride, tributylstannyl isocyanate, bistributylstannylcarbodi-imide, and a polymer of 6-chlorohexyl isocyanate[200].

The structure of the equimolecular adducts of phenyl isocyanate with trimethyl- and triphenyl-stannylcyanamide has not been established with certainty. It is supposed[123,139] that the stannyl group can add both to nitrogen and to oxygen atoms. More definite conclusions have been reached[123,190] concerning the structure of the products of the action of phenyl isothiocyanate on bistriphenylstannylcarbodi-imide (in benzene at 26 °C):

$$Ph_3SnN{=}C{=}NSnPh_3 + PhN{=}C{=}S \rightarrow \rightarrow \begin{matrix} PhN{=}C{-}SSnPh_3 \\ | \\ Ph_3SnN{-}C{\equiv}N \end{matrix} \xrightarrow{H_2O} \begin{matrix} PhN{=}C{-}SSnPh_3 \\ | \\ HN{-}C{\equiv}N \end{matrix}.$$

An organotin derivative of cyanoisothiourea can be obtained also by the action of phenyl isothiocyanate on triphenylstannylcyanamide:

$$Ph_3SnNHCN + RN{=}C{=}S \rightarrow \begin{matrix} RN{=}C{-}SSnPh_3 \\ | \\ HN{-}C{\equiv}N \end{matrix}.$$

The rate of the reaction increases with the nature of the radical in the isothiocyanate in the sequence[123,190]

$$p\text{-}O_2NC_6H_4NCS > PhNCS > PhCH_2NCS \sim$$
$$\sim p\text{-}EtOC_6H_4NCS > EtNCS.$$

N-Triphenylmethyl-*N'*-triphenylstannylcarbodi-imides had not reacted with an isothiocyanate in ether at 28 °C after 23 h.[123]

Trialkylstannylcyanamides react with yet another hetero-cumulene system--carbon disulphide[50]:

$$R_3SnNHCN + CS_2 \rightarrow HN{=}\underset{\underset{NH_2}{|}}{C}{-}NHC{\equiv}N + R_3SnSSnR_3 + NCN{=}\underset{\underset{NC{-}NSnR_3}{|}}{C}SSnR_3$$

R=Me, Ph, $PhCH_2$.

It has been reported also[117] that organogermanium carbodi-imides do not react with carbon disulphide.

V. ASPECTS OF PRACTICAL APPLICATION

Hetero-organic carbodi-imides and cyanamides have recently begun to find practical application in the synthesis of various polymers and difficultly accessible organic compounds, as well as in certain industrial chemical processes. Thus bistrimethylsilylcarbodi-imide has been successfully tried as a moisture stabiliser for polyurethanes based on complicated polyesters employed for the production of artificial leather and other purposes[203]. It has been proposed as a substitute for the most widely used for these purposes, 2,2,6,6-tetraisopropyldiphenylcarbodi-imide (Stabaksol 1). Oligomers and polymers containing a carbodi-imide group in the macromolecular chain, obtained by the interaction of organosilicon diols and isocyanatocarbodi-imides, are used for the stabilisation of polyester–urethanes to moisture and heat. Additions of 0.1–3% to polyurethanes significantly enhance their resistance to high temperatures and moisture[204].

Polymeric organosilicon carbodi-imides, obtained by the action of polychlorosilanes or chlorosilanes on bisdimethylsilylcarbodi-imide, can be used as insulating coatings, components of high-temperature colorants, etc., in cases in which high heat resistance is required[118–121]. Furthermore, such polymers are stable to irradiation, which permits their use in various types of packing operating under conditions of intense irradiation. For example, polysilylcarbodi-imide $[(C_6H_5)_2SiNCN]_n$ of molecular mass 4285 undergoes no loss in weight when heated in nitrogen to 400 °C, and retains its elasticity when exposed to an [electron irradiation] dose of 2000 MR g^{-1}.[118–121]

Organotin carbodi-imides have been suggested as heat stabilisers for polyvinyl chloride compositions[205,206]. They are also effective catalysts for urethane formation[207–211]. Thus bistributylstannylcarbodi-imide has been used as catalyst for the preparation of film-forming polyurethane coatings based on organosilicon polyols and aliphatic polyisocyanates of biuret structure[209]. Bistrimethylsilylcarbodi-imide is also a heat stabiliser for polyvinyl chloride, but considerably less effective than organotin carbodi-imide[212].

Organotin cyanamide derivatives possess antibacterial activity[139,188]. Organolead cyanamides of type $(CH_3)_3.PbNHC{:}N$ are employed as extremely efficient antioxidants and additives in lubricating and engine oils[51,213].

Hetero-organic carbodi-imides can also be employed as intermediates in the synthesis of various difficultly accessible organic compounds, e.g. dialkylcyanamides[112,122] and 1,3,5-triazines[138,194,195,197,199].

There is no doubt that the fields of practical application of hetero-organic cyanamides and carbodi-imides of Group IVB elements have not been fully studied. Further, more thorough investigation of the chemical properties of these interesting compounds will make it possible to extend considerably the range of their practical application.

* * *

During preparation of this Review for the press additional publications have appeared on the synthesis[214–219] and properties[219–221] of organosilicon and organogermanium carbodi-imides.

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Oxidation of Organometallic Compounds by Transition Metal Salts

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The mechanisms of one- and two-electron oxidation of organometallic compounds by transition metal salts are considered. It is shown that organometallic compounds can be oxidised as a result of dielectric electron transfer but usually unstable transition metal compounds are formed as intermediates in the reactions. The mechanisms of the thermal and catalytic decomposition of certain types of organometallic compounds are discussed in this connection.
The bibliography includes 244 references.

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I. INTRODUCTION

The reactions of organometallic compounds with transition metal salts have continuously attracted the attention of investigators because many of them are of preparative value. Recently interest in such reactions has increased still further in connection with their involvement in complex processes catalyses by transition metal complexes.

Various reactions occur when organometallic compounds interact with transition metals salts. These include in the first place the transmetallation reaction as a result of which a new organometallic compound is formed:

$$RMX_n + M'X_n \rightarrow RM'X_{m-1} + MX_{n+1} . \quad (1)$$

Since this review is devoted to reactions involving the oxidation of organometallic compounds, we shall consider only those in which unstable organometallic intermediates, decomposing with formation of the products R_2, RH, and R(-H), are formed.

According to modern ideas, organic compounds of transition metals can decompose via the free-radical mechanism (2) and via the so-called bimolecular mechanism (3) in which free radicals are not formed:

$$RM'X_{m-1} \rightarrow R^{\cdot} + M'X_{m-1} ,$$
$$2R^{\cdot} \rightarrow RH + R(-H) , \quad (2)$$
$$2R^{\cdot} \rightarrow R_2 ;$$

$$2RM'X_{m-1} \rightarrow RH + R(-H) + 2M'X_{m-1} ,$$
$$2RM'X_{m-1} \rightarrow R_2 + 2M'X_{m-1} . \quad (3)$$

Whereas the free-radical mechanism of the decomposition of organometallic compounds is understood in all its aspects, the question of the essential features of the bimolecular mechanism is not quite so clear and there is not even a unanimous view concerning the nature of the reactions occurring. For example, it is not clear how the organometallic compounds decompose in this instance, whether the process is homolytic and occurs within a radical cage or whether it is heterolytic

and involves, for example, the hydride elimination stage whose products are RH and R(−H). This uncertainty has resulted in the lack of a single terminology used to designate this mechanism. It is referred to as the bimolecular mechanism, the latent radical mechanism, and sometimes the latent ionic mechanism, but these terms merely confirm the absence of free radicals.

When organometallic compounds interact with metal salts, free radicals can be formed not only as a result of the homolytic decomposition of the product of the transmetallation reaction (2) but also in the one-electron oxidation of the organometallic compounds. The radicals formed in this instance, as in mechanism (2), dimerise, disproportionate, or react with the solvent:

$$RMX_n + M'X_m \rightarrow [(RMX_n)^+ (M'X_m)^-] \rightarrow R^\cdot + MX_{n+1} + M'X_{m-1} ,$$
$$2R^\cdot \rightarrow R_2 ,$$
$$2R^\cdot \rightarrow RH + R(-H) . \qquad (4)$$

This pathway, leading to the oxidation of organometallic compounds, is fundamentally different from mechanism (2) discussed above. On the other hand, they are difficult to distinguish because the reaction results in the formation of free radicals and the same products. Finally, when organometallic compounds interact with metal salts, there is a possibility of two-electron oxidation to carbonium ions R^+, which react with nucleophilic species via mechanism (5). Carbonium ions can be formed in these reactions in a wide variety of ways: in the intramolecular decomposition of $RM'X_{m-1}$ [mechanism (5), pathway *a*] produced as a result of transmetallation in accordance with Eqn.(1), in the oxidation of the radicals $R^\cdot$ [mechanism (5), pathway *b*] generated via pathways (2) and (4), or in the direct two-electron oxidation of the initial organometallic compound [mechanism (5), pathway *c*]:

$$RM'X_{m-1} \xrightarrow{a} R^+ + M'X_{m-2} + X^- ,$$
$$R^\cdot + M'X_m \xrightarrow{b} R^+ + M'X_{m-1} + X^- ,$$
$$RMX_n + M'X_m \xrightarrow{c} R^+ + MX_{n+1} + M'X_{m-2} + X^- ,$$
$$R^+ + Nu^-(X^-) \rightarrow RNu(RX) . \qquad (5)$$

We may note that free carbonium ions are not always formed in the two-electron oxidation of organometallic compounds—for example, when electron transfer takes place with the simultaneous transfer of a nucleophilic ligand:

$$RM'X_{m-1} \xrightarrow{a} RX + M'X_{m-2} ,$$
$$R^\cdot + M'X_m \xrightarrow{b} RX + M'X_{m-1} ,$$
$$RMX_n + M'X_m \xrightarrow{c} RX + MX_{n+1} + M'X_{m-2} . \qquad (6)$$

There is also a possibility of a rarely encountered activation of the intramolecular transfer of a second electron as a result of the attack by the nucleophile (Nu) on the radical-cation intermediate:

$$RMX_n + M'X_m \rightarrow (RMX_n)^+ + M'X_{m-1} + X^- ,$$
$$(RMX_n)^+ + Nu^- \rightarrow RNu + MX_n . \qquad (7)$$

This review deals with the above mechanisms of the oxidation of organometallic compounds by metal salts. To facilitate exposition, the data for reactions involving the oxidation of organometallic compounds by silver(I), copper(I), and copper(II) salts as well as Group VIII metal salts are considered as far as possible in separate sections. This is mainly because specific mechanisms have been proposed for each oxidant and numerous examples of their reactions have been studied. Analogous problems are dealt with also in recently published reviews[1,2].

In our view, the thermal decomposition reactions of organic derivatives of silver, copper(I), and other transition metals also merit attention. Interest in these processes is due to two causes. Firstly, they may constitute the stage in which the intrinsic oxidation of the organic group R occurs. This happens when the oxidation of an organometallic compound by the metal salt begins with the transmetallation reaction and an intermediate RM is formed. Secondly, these reactions are oxidation processes of a specific type for which independent mechanisms have been proposed. We shall adhere to these standpoints in considering the wide variety of decomposition reactions of organometallic compounds. Thus we shall regard the homolytic decomposition of organometallic compounds as a one-electron oxidation process. This is not a formal approach, since the carbanion bound to the metal cation is indeed oxidised in the course of the reaction, being converted into a radical. Similarly the decomposition of the compounds RM with formation of R^+ or intramolecular decomposition of R_2M with formation of R_2, RH, and R(−H) should be regarded as two-electron oxidation processes. These reactions are considered in detail in the last section of the present review.

II. ONE-ELECTRON OXIDATION OF ORGANOMETALLIC COMPOUNDS BY TRANSITION METAL SALTS

Particularly numerous reactions with transition metal salts are known for organomagnesium compounds RMgX. In many instances, especially for R = Ar, this reaction can serve as a preparative method for the synthesis of biaryls, since in the synthesis of a symmetrical product this reaction is simpler than the Wurtz–Fittig reaction.

The reaction (with a nearly quantitative yield of biaryl) was first carried out in 1914:[3]

$$p\text{-}MeC_6H_4MgBr \xrightarrow[80-85\%]{CrCl_3} (p\text{-}MeC_6H_4)_2 .$$

In subsequent years the number of examples of similar reactions increased and studies were mainly carried out in order to elucidate the influence of the nature of the metal salt on the yield of product. It was shown[4] that the yield of biphenyl (%) varies as follows as a function of the nature of the oxidant in the reactions of PhMgI with metal salts in ether:

$FeCl_2$	98	$PdCl_2$	98
$CoBr_2$	98	$OsCl_3$	53
$NiBr_2$	100	$IrCl_3$	28
$RuCl_3$	99	$PtCl_4$	5
$RhCl_3$	97	—	—

According to Tsutsui[5], the yield of the dimerisation product (%) in the reaction of ArMgX with various metal chlorides in tetrahydrofuran (THF) varies within a very wide range:

$FeCl_2$	47	$MnCl_2$	21
$CoCl_2$	86	$CrCl_3$	7
$NiCl_2$	72	$CuCl_2$	6

Biaryls are formed when arylmagnesium bromides are treated with thallium(I) bromide[6], uranyl nitrate[7], titanium tetrachloride and vanadium oxide trichloride[8], and chromium(IV) t-butoxide[9]. Depending on the nature of the aryl group, the yield of the dimerisation product varies for the majority of salts from 25 to 100%.[8]

When transition metal salts act on alkylmagnesium halides, the main products become olefins and alkanes and not coupling products[10]. The yields of the products of these reactions have been reported[11]. Cotton[12] proposed the following

classification of the reactions taking into account the preferential formation of particular products: mainly alkanes in group I reactions, disproportionation products in group II reactions, and alkanes and olefins together with coupling products in group III reactions, while group IV reactions include those whose products are the dimers Alk_2. According to this classification, transition metal salts are involved mainly in reactions to the following types:

group I: $TiCl_4$, $Ti(OR)_4$, $ZrCl_4$, $TaCl_5$;
group II: $CrCl_3$, $MnBr_2$, $FeCl_2$, TlCl, Cu_2Cl_2, $CuCl_2$;
group III: AgX, $AuCl_3$.

Group IV reactions are those of silver and copper salts with organomagnesium and organolithium compounds without a β-hydrogen atom.

The mechanisms of the reactions of transition metal salts with aryl- and alkylmagnesium halides are usually regarded as consecutive transmetallation and decomposition of the organometallic intermediate by a radical mechanism or without the involvement of free radicals. It is believed[11] that the decomposition of the organometallic intermediate can be unimolecular [radical mechanism (2)] or bimolecular [without the involvement of radicals—mechanism (3)]. The decomposition of aliphatic organometallic derivatives containing a β-hydrogen atom apparently takes place via a hydride abstraction stage. This case will be examined below.

A detailed study of the products of the reactions of organomagnesium compounds with transition metal salts was first undertaken by Smith[13] in order to elucidate the mechanism of the decomposition of organometallic intermediates. It was found that, when cobalt(II) bromide reacts with PhMgBr, benzene (42%) and biphenyl (45%) are formed, whereas in the case of p-MeC_6H_4MgBr the products are toluene (55%) and bitolyl (33%). On the other hand, when a mixture of these Grignard reagents (PhMgBr and p-MeC_6H_4.MgBr) is treated with $CoBr_2$, an asymmetric biaryl resulting from cross-coupling is formed together with the above products, the relative yields of the biaryls (%) differing from the statistical distribution: PhH (53)†, Ph_2 (30), PhMe (55), $(p\text{-}MeC_6H_4)_2$ (18), and PhC_6H_4Me (15). This result alone provides grounds for the hypothesis that the biaryls are not formed from free radicals.

When $CoBr_2$ reacts with a mixture of aryl and alkyl Grignard reagents (PhMgBr and EtMgBr), mainly benzene, ethane, and ethylene are formed, whereas the amount of cross-coupling products obtained is small[13]: PhH (81)†, Ph_2 (16), PhEt (5), EtH (52), C_2H_4 (47), and BuH (1).

In addition, the ratio of the alkanes and alkenes formed is smaller than in the reaction of individual alkylmagnesium bromides. In its turn the amount of benzene formed in this instance is greater than in the reaction of PhMgBr with $CoBr_2$ while that of biphenyl is actually smaller. According to Smith[13], this can be associated with the additional disproportionation reaction between the phenyl and alkyl derivatives of cobalt(II).

The results presented undoubtedly indicate a bimolecular mechanism of the decomposition of the intermediates or at least an appreciable contribution of this reaction pathway to the overall process. The data obtained by Wittig for the reactions of 2,2'-dilithiobiphenyl [14] or o-dilithiobenzene [15] with transition metal salts agree with this view. Thus o-dilithiobenzene gives rise to biphenyl and triphenylene (in an overall yield up to 25%), their relative yields depending on the nature of the salt employed. We may note that dehydrobenzene is not formed in this reaction and triphenylene could not therefore be produced as a result of its trimerisation.

The only product of the reaction of PhMgBr with cobalt(III) and manganese(III) acetylacetonates is biphenyl[16], whose yield is independent of the added α-methylstyrene. The operation of the bimolecular mechanism is apparently due to the fairly high stability of the aryl derivatives of cobalt(III) and manganese(III).[12,17]

In principle, a free-radical mechanism is also possible for the reactions of organomagnesium compounds RMgX with transition metal salts. Both the formation of the hydrocarbons RH in a series of reactions as well as the presence of deuterium in the products of the reaction of PhMgBr with various salts in a mixture of deuterated benzene and ether can serve as confirmation of this postulate[18]. The radicals can be formed in these reactions on homolytic decomposition of the transmetallation product or as a result of the one-electron oxidation of the organomagnesium compound. The available data are usually insufficient to make an unambiguous choice between the possible pathways leading to the formation of the reaction products. It has been shown convincingly in only one study[19] that radicals are formed in the reaction of alkyl-lithium with $TiCl_4$ as a result of electron transfer and not on decomposition of $RTiCl_3$, because the above compound is stable under the experimental conditions.

Like the aryl derivatives, aliphatic organomagnesium compounds react with transition metal salts apparently with formation of unstable organometallic compounds. It has been shown[20] that, when EtMgBr is treated in THF with palladium(II), copper(II), and copper(I) salts, the ratio of the products formed (ethane and ethylene) is close to unity. On treatment with iron(II), iron(III), cobalt(II), nickel(II), and manganese(II) salts, the ethane : ethylene ratio varies in the range 2–5,[20,21] but in the presence of styrene the yields of ethane and ethylene become identical and the yield of butane increases. According to the authors[20], styrene plays the role of a π-ligand and stabilises the organometallic intermediate; this reduces the probability of the homolytic decomposition, as a result of which the reaction proceeds via a bimolecular mechanism.

In the reaction involving the oxidation of two organomagnesium compounds (RmgX and R'MgX) containing a β-hydrogen atom the yield of the cross-coupling products is appreciable only for copper and silver salts, while in the remaining instances disproportionation products are formed. It is of interest to note that the ratio of alkanes and alkenes formed from RMgX depends on the nature of the R'MgX. Thus, in the interaction of ethyl- and n-propyl-magnesium bromides with palladium chloride, the ratio $C_2H_4/C_2H_6 = C_3H_6/C_3H_8 = 0.9$, while in the reaction of ethyl- and isopropyl-magnesium bromides $C_2H_4/C_2H_6 = 0.4$ and $C_3H_6/C_3H_8 = 2.6$, i.e. the alkane is formed mainly from the ethyl group, while the olefin is formed from the propyl group. An analogous behaviour has been observed for other transition metal salts, but the differences between the ratios of products are not so significant.

Two possible mechanisms of the formation of alkanes and alkenes in these reactions were considered[20]:

(1) the hydride mechanism[21]:

$$RCH_2CH_2M \rightarrow RCH{=}CH_2 + MH \quad ,$$
$$RCH_2CH_2M + MH \rightarrow RCH_2CH_3 + 2M \quad ;$$

(2) the bimolecular mechanism:

$$2RCH_2CH_2M \rightarrow RCH{=}CH_2 + RCH_2CH_3 + 2M \quad .$$

The authors[20] believe that organometallic intermediates formed in many reactions decompose with participation of the

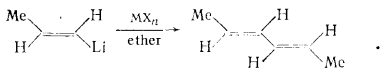
† The yields of the reaction products are calculated taking into account the overall concentration of Grignard reagents.

metal hydride. Reactions of organometallic compounds with copper(I) and silver salts, particularly in the case of secondary and tertiary derivatives, are an exception[22].

One of the distinctive features of vinyl Grignard reagents or organolithium compounds in reactions with transition metal salts is their tendency to form dimerisation products. However, the yield of the latter depends greatly on the nature of the metal salt. Thus the yield of hexa-2,4-diene in the reaction of *trans*-propenyl-lithium in ether varies as follows as a function of the salt[23]:

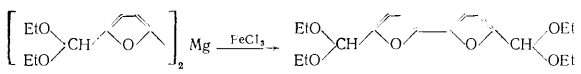
MX_n	$ZrCl_4$	$CrCl_2$	VCl_3	$PdCl_2$	$FeCl_2$	$CrCl_3 \cdot 3THF$	$MnBr_2$	$CoCl_2$	$(Ph_3P)_2PtCl_2$	MoCl
Yield, %	2	9	24	24	25	47	49	73	115	176

The reaction is to a large extent stereospecific even in those cases when the yield of hexa-2,4-diene is low. The reaction mechanism apparently involves the bimolecular decomposition of vinyl derivatives of metals. According to the authors[23], the high stereospecificity of the reaction is due to the involvement of the π-bond in the stabilisation of the configuration of the transition state:



Biaryls are apparently formed in reactions of aryl Grignard reagents with transition metal salts also on bimolecular decomposition of the intermediates. For example, the fact that the yield of biphenyl reaches 70% in the interaction of PhMgBr with $FeCl_3$ in ether at −80 °C, while chlorobenzene and an appreciable amount of tarry products are formed at the usual temperatures is consistent with this view[24]. One cannot rule out the possibility that at room temperature the intermediate undergoes the usual homolytic decomposition and not bimolecular decomposition and the phenyl radicals formed are oxidised to chlorobenzene. Such a decrease of the relative yield of the dimer with increase of temperature was observed for the reaction of $CoBr_2$ with a neophyl Grignard reagent without a β-hydrogen atom[25].

Organomagnesium derivatives of the furyl series are oxidised by transition metal salts with formation of dimerisation products. Thus treatment of bis(2-diethoxymethyl-5-furyl)-magnesium with iron(III) chloride results in a quantitative yield of bis-2,2′-diethoxymethyl-5,5′-bifuryl[26]:



Organoaluminium compounds react fairly readily with transition metal salts. When triethylaluminium is treated with cobalt(II) chloride in ether, ethane and ethylene are formed in nearly unimolecular proportions (51.5 : 48).[27] At a higher temperature, for example on refluxing in methylcyclohexane, the yield of the alkane increases to 69%, which may be associated with the homolytic decomposition of the organocobalt intermediate. When trimethylaluminium interacts with cobalt(II) acetylacetonate in benzene, methane and ethane are mainly formed (in proportions of 3 : 1) together with a small amount of toluene[28]. The authors[28] believe that toluene is the product of heterolytic substitution in which the intermediate $CH_3Co(acac)_2$ participates, and it is most probably formed on radical methylation of benzene.

The reactions of triethylaluminium with cobalt(III), chromium(III), and iron(III) acetylacetonate complexes have been investigated in fair detail[29,30], because these systems are used to initiate the polymerisation of monomers. The formation of nickel(I) compounds has been detected by EPR in the reaction involving a nickel(II) complex.[31]

Organometallic compounds having a more covalent C–M bond than the compounds of alkali and alkaline earth metal metals also react fairly readily with transition metal salts. For example, Razuvaev and coworkers have shown that, when diphenylmercury is refluxed with iron(III), cobalt(II), manganese(II), and nickel(II) chlorides in dioxan, ethylcellosolve, or pyridine, the product is benzene. Biphenyl was not detected among the products[32,33]. The intermediates formed apparently decompose under the reaction conditions via a free-radical mechanism and the phenyl radicals react with the solvent. At a lower temperature the stability of the intermediates increases and, as already shown for reactions with active organometallic compounds, a bimolecular decomposition mechanism operates in this instance and a biphenyl is formed.

In the reaction of diphenylmercury with highest-valence vanadium compounds ($VOCl_3$ and VCl_4) in cyclohexane, biphenyl is formed[34], i.e. the intermediates decompose via a bimolecular mechanism. This is also indicated by the finding that, for the equimolar reactant ratio, these reactions do not induce the polymerisation of ethylene. However, in the presence of an excess of diphenylmercury relative to the oxidant, polyethylene with a low molecular weight is formed, which the authors[34] believe to be due to the homolytic decomposition of vanadium derivatives containing several phenyl groups.

When dibenzylmercury or benzylmercury chloride is oxidised with iron(III), cobalt(II), and copper(II) chlorides, benzyl chloride is formed[35]:

$$PhCH_2HgCl + FeCl_3 \rightarrow PhCH_2Cl + HgCl_2 + FeCl_2 \quad .$$

The authors[35] believe that the reaction has a latent ionic mechanism (free radicals are not formed in the reaction). These two-electron oxidation reactions will be examined in greater detail below.

The reactions of di-isopropylmercury with titanium(IV), iron(III), cobalt(II), and tin(IV) chlorides result in the formation of isopropyl radicals, because the acrylonitrile added to the reaction mixture polymerises under these conditions[36]. However, it is difficult to agree with the authors[36] that this is evidence for the one-electron transfer mechanism because the radicals might have been formed as a result of the homolysis of the intermediate formed.

The main product of the reaction of di(*p*-tolyl)mercury with $Pd(OAc)_2$ or of *p*-tolylmercury acetate with $PdCl_2$ is bitolyl[37]. Heterocyclic organomercury compounds react similarly[38]. The formation of biaryls in the reaction of substituted arylmercury salts with palladium(II) chloride proceeds equally well in the presence of both electron-donating and electron-accepting substituents[39]. The reaction was patented as a method of synthesis of biaryls as a result of the oxidative coupling of organomercury salts and was modified in such a way that the palladium(II) salts functioned as the catalyst and the oxidant was $CuCl_2$:[39]

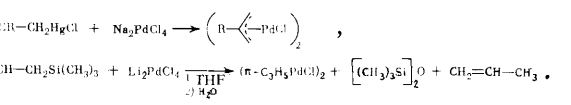
$$p\text{-}MeC_6H_4HgCl \xrightarrow[AcOH]{PdCl_2\text{-}CuCl_2} (p\text{-}MeC_6H_4)_2 \quad .$$

The interaction of arylboronic acids with palladium salts should be included among the oxidative coupling reactions of the type considered[40]. A common feature of all these reactions is that they apparently proceed via a transmetallation stage and subsequent bimolecular decomposition of organopalladium intermediates:

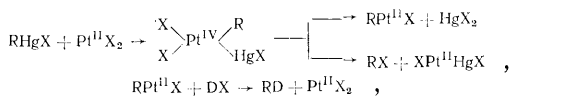
$$RHgX + PdX_2 \rightarrow RPdX + HgX_2 \quad ,$$
$$2RPdX \rightarrow R_2 + PdX_2 + Pd \quad .$$

When the organopalladium intermediate is relatively stable, the reaction stops at the transmetallation stage. For example, when allyl derivatives of metals are treated with palladium(II)

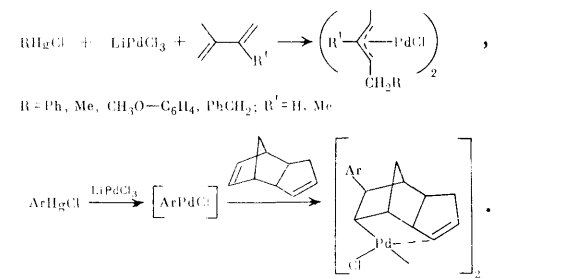
chloride, a stable dimer of π-allylpalladium dichloride is formed[41,42]:



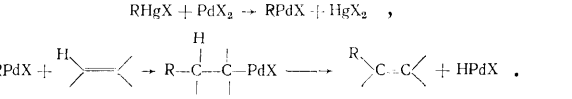
On the other hand, if the palladium intermediate is unstable, its formation can be inferred from the products formed following the addition of special reagents or on reaction with the solvent. For example, it has been shown that[43] the protolysis of alkylsilanes is catalysed by palladium(II) and platinum(IV) salts. Transmetallation leads to the formation in the reaction of organometallic intermediates, which undergo protolysis. The formation of platinum intermediates in the reaction of RHgBr (R = Me, Et, or Bu) with K_2PtX_4 (X = Cl or Br) may be postulated analogously[44]. The reaction was carried out in a D_2O–MeCOOD mixture, in which organomercury compounds are stable, but, after the addition of platinum salts, deuterated hydrocarbons and alkyl halides were formed. It has been suggested that the reaction proceeds via an oxidative addition stage:



Olefins are specific agents trapping the unstable organopalladium intermediates. The reaction involving addition to a multiple bond results in the formation of a new organopalladium compound which can be isolated if it is sufficiently stable[45–47]:



The reaction continues in an interesting manner when the organopalladium intermediate is not stabilised by ligands and contains a β-hydrogen atom. The elimination of palladium hydride then results in the formation of a substituted olefin[46]:

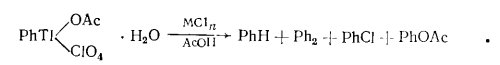


This reaction, discovered by Heck and given his name, is of preparative value as a method of arylating olefins[46,48–50].

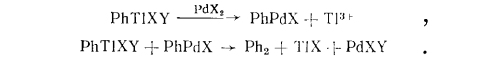
Another compound whose reaction can serve as a test for the formation of palladium intermediates is carbon monoxide. For example, alkyl carboxylates and ketones are formed in alcohol in the presence of CO.[51] However, in the presence of a very large excess of the olefin or CO, the bimolecular decomposition of intermediates is not fully suppressed, although the yield of a dimeric product diminishes[51,52].

Apparently there exists also another pathway in the reaction of organometallic compounds with palladium(II) salts in which there is no transmetallation stage. Thus the composition and yield of the products of the reaction of bis(allylpalladiumchloride) with organic derivatives of Group IVB elements depend on the nature of the metal[53]. It has therefore been suggested that the oxidation proceeds in the complex of R_4M with $(\pi\text{-}C_3H_5PdCl)_2$.

In the reaction of the organothallium compound PhTl(OAc).$.ClO_4.H_2O$ with $PdCl_2$, benzene and biphenyl are formed on refluxing in acetic acid[54]. If the same reaction is carried out in the presence of catalytic amounts of other transition metal chlorides (117 °C, 5 h), then chlorobenzene and phenyl acetate are formed together with biphenyl[55]:

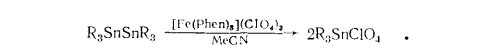


We may note that, with the exception of biphenyl, all these products might be formed in the presence of metal salts either as a result of acetolysis or as a result of the oxidative elimination of thallium. The mechanism of the formation of biphenyl, whose yield depends on the nature of the catalyst employed, is more complex. It is believed[55] that the poor reproducibility of the yield of biphenyl in the reactions involving iron(II), thallium(III), and copper(II) chlorides indicates a radical reaction mechanism. Presumably the intermediate $PhMCl_{n-1}$, formed as a result of transmetallation, undergoes homolytic decomposition and the catalyst is regenerated when MCl_{n-1} is oxidised with tervalent thallium. At the same time one cannot rule out the possibility of the formation of biphenyl also without the involvement of free radicals, as has been suggested, for example, for the reaction of organothallium compounds with $PdCl_2$:[55]

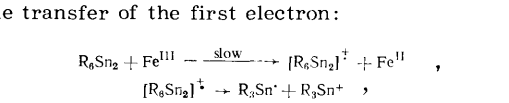


This reaction pathway resembles very closely the bimolecular decomposition of organometallic compounds discussed above and formally constitutes two-electron oxidation.

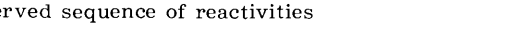
It is seen from the data presented above that the commonest mechanism of the oxidation of organometallic compounds by a transition metal salt involves consecutive transmetallation stages and thermal decomposition of the intermediates formed. However, there exist processes in which oxidation takes place as a result of intermolecular electron transfer. Such reactions are particularly characteristic of organobimetallic compounds and π-bonded transition metal compounds—for example the oxidation of distannanes R_3SnSnR_3 (R = Me, Bu, or Ph) by compounds of iron(III) perchlorate with phenanthroline[56] or other complex-forming agents[57] in acetonitrile:



The reaction is of second order overall and of first order with respect to each reactant and the slow stage is apparently the transfer of the first electron:

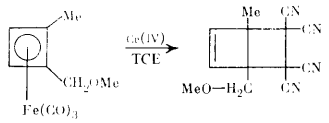


The observed sequence of reactivities

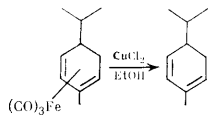


reflects the electron-donating capacity of these compounds relative to the oxidant. The satisfactory linear correlation between $\lg k_2$ and $E^0(Fe^{III}L_n/Fe^{II}L_n)$ with a slope $\alpha = 0.44$ suggests that electron transfer proceeds via an outer-sphere mechanism[56]. Processes such as the interaction of silver

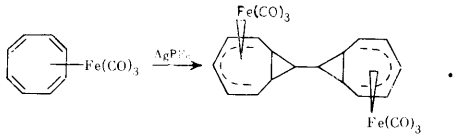
salts with the distannanes R_6Sn_2 [58] and diplumbanes[59] or the oxidation of π-bonded transition metal compounds should apparently be considered within the framework of the oxidation-reduction mechanism. Thus the oxidation of substituted cyclobutadieneiron tricarbonyl by cerium(IV) leads to the formation of a substituted cyclobutadiene, which can be trapped by tetracyanoethylene (TCE):[60]



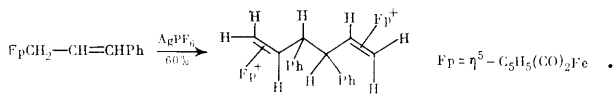
The dienyl complexes of $Fe(CO)_3$ are oxidised similarly by copper(II) chloride[61]:



Whereas the iron atom is oxidised in the above reactions of dienyl complexes of $Fe(CO)_3$, in the interaction of the η^4-cyclo-octatetraenyl complex with silver hexafluorophosphate only the organic ligand is oxidised and a new organometallic compound is formed[62]:



The oxidation of allyl σ-derivatives of cyclopentadienyliron dicarbonyl is the same type of reaction[63]:



We may note that in this case both the organic group and the organometallic fragment are oxidised. The intermediate formation of allyl radicals in this reaction has been confirmed by the finding that the π-olefin cation (Fp^+-π-CH_2=CR^1-CR^2R^3H), which is a product of the reaction of the radical with a solvent, is formed together with the dimer.

III. OXIDATION OF ORGANOMETALLIC COMPOUNDS BY SILVER AND COPPER SALTS

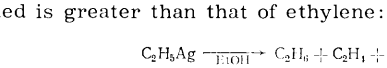
We shall consider the reactions involving the oxidation of organometallic compounds by salts of the copper subgroup metals: Cu, Ag, and Au. These reactions are of interest because many of them, particularly those involving copper(I) salts, are widely used in organic synthesis[63].

1. Reactions of Organometallic Compounds with Univalent Silver Salts

It is well known that the interaction of organometallic compounds with silver salts results in the formation of organosilver compounds which are usually unstable and yield on decomposition the radical coupling products[65]. Thus the reactions of Grignard reagents RMgX (for example, with R = Ar, $PhCH_2$, or Bu) with silver salts lead to the formation of the hydrocarbon R_2, whose yield is frequently quantitative[66,67]. Apart from the coupling product R_2, the reactions of isobutyl- and s-butyl-magnesium bromides results in the formation of a small amount of butene and butane[68]. It has been shown that the reaction of $RPbEt_3$ (R = p-$CF_3C_6H_4$, p-$Me_2NC_6H_4$, PhCH=CH, etc.) involves the cleavage of the bond and the formation of an organosilver compound which then decomposes to R_2.[69] The reactions of benzyl and allyl derivatives of lead result directly in the formation of R_2. The intermediate formation of organosilver compounds cannot be detected in this instance because they are extremely unstable. In the reaction of vinyl derivatives of lead, mono-olefins are obtained together with hydrocarbons[70,71].

Thus the reactions of organometallic compounds with silver salts as a rule begin with transmetallation. This view gives rise to no doubts at the present time and the problem therefore consists in establishing the mechanism of the thermal decomposition of the organosilver compounds. Numerous investigations in this field have shown that RAg can decompose via a bimolecular mechanism, i.e. without the involvement of free radicals[22,72,73], and via a free-radical mechanism[69,74–77]. The relative contributions of these reaction pathways are in general determined both by the nature of the group R and by the reaction conditions. We shall consider the problem in relation to the thermal decomposition reactions of alkyl, vinyl, and aryl derivatives of silver.

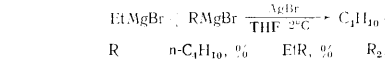
The radical mechanism of the thermal decomposition of organosilver compounds was first proposed for ethylsilver[78] and was subsequently confirmed as a result of a study of the kinetics of this reaction[74]. The main evidence in support of the formation of radicals is that the amount of ethane formed is greater than that of ethylene:



The ratios of the yields of C_2H_6, C_2H_4, and C_4H_{10} are 2.5 : 0.38 : 0.37.[74] There is no doubt that ethane is a product of the reaction of the ethyl radical with the solvent#. An analogous behaviour has been observed in the reaction of Et_4Pb with $AgNO_3$ in which ethylsilver is obtained as an intermediate, while ethane, ethylene, and butane are formed in ratios of 53.2 : 9.9 : 36.2.[72]

At the same time, there are data which do not agree with the free-radical mechanism of these reactions. For example, the reaction of tetramethyl-lead with $AgNO_3$ results in the formation of ethane; methane has not been detected among the reaction products[78]. Furthermore, styrene, methyl methacrylate, or acrylonitrile added to the reaction mixture do not polymerise under the reaction conditions[76].

A widely used procedure, with the aid of which investigators have frequently attempted to determine the mechanism of the decomposition of organosilver compounds, consists in carrying out simultaneously the reactions of the silver salt with two different Grignard reagents and subsequent analysis of the reaction products. Thus the interaction of silver bromide in THF with ethylmagnesium bromide mixed with other alkylmagnesium bromides results in the formation of the following coupling products[79]:



R	n-C_4H_{10}, %	EtR, %	R_2, %	Σ, %
Et	46	46	--	92
Pr	47	37	12	96
iso-Pr	41	28	10	79
t-Bu	36	5	19	60

The data presented show that in the case of normal alkylmagnesium bromides the overall yield of coupling products is also quantitative. The amount is somewhat smaller in the

It has been shown that the radical abstracts hydrogen from the hydroxy-group of the alcohol but in the decomposition of methylsilver more hydrogen is abstracted from the α-CH bond[77].

reaction with Grignard reagents having a branched group R, which is apparently associated with the formation of alkanes and alkenes in side reactions. It is also striking that, with increase of the degree of branching in the group R in the Grignard reagent, the yield of cross-coupling products diminishes from 46% to 5%, while the yield of homocoupling products R_2 not only does not diminish but actually increases. These data are difficult to account for from the standpoint of the free-radical mechanism.

The most convincing evidence for the possibility of a bimolecular mechanism of the decomposition of alkyl derivatives of silver has been obtained by Clinton and Kochi[80], who investigated the reaction of tetraethyl-lead with silver triflate in THF. It was found that the ratio of the ethane, ethylene, and butane formed in this instance depends on the concentration of the silver salt and that in the presence of oxygen the yield of ethane is significantly reduced, while that of butane remains almost unaltered. Evidently ethane is formed predominantly via a radical pathway, while butane results from the bimolecular reaction

$$2EtAg \rightarrow BuH + 2Ag \quad .$$

In contrast to free alkyl derivatives of silver, the tributylphosphine complex of n-butylsilver is more stable and decomposes in ether with formation of octane (93%) and insignificant amounts of butane (5%) and butene (2%).[22] According to the authors[22], the C–Ag bond dissociates in this instance with simultaneous formation of a new C–C bond, while the contribution of the radical reaction pathway is insignificant. Furthermore, silver(I) hydride is apparently not involved in the formation of the disproportionation product, because the yield of butane is higher than that of butene. However, one cannot rule out the possibility that the thermal decomposition of s-BuAg(PBu_3) does in fact proceed via a stage involving the formation of AgH, since all the products (butane, butene, and octane) are obtained in comparable amounts and, furthermore, the amount of butene is greater than that of butane:

$$\underset{29\%}{\text{s-BuAg}(PBu_3)} \rightarrow \underset{35\%}{BuH} + \underset{30\%}{C_4H_8} + C_8H_{18} + Ag + PBu_3 \quad ,$$

$$RAg(PBu_3) \rightarrow R(-H) + HAg(PBu_3) \quad ,$$

$$RAg(PBu_3) + HAg(PBu_3) \rightarrow RH + Ag + PBu_3 \quad ,$$

$$2RAg(PBu_3) \rightarrow R_2 + Ag + PBu_3 \quad ,$$

$$2HAg(PBu_3) \rightarrow H_2 + Ag + PBu_3 \quad .$$

It is seen from the data presented that the alkyl derivatives of silver can decompose via both radical and bimolecular mechanisms. Vinyl organosilver compounds decompose similarly. For example, the interaction of triethylisobutenyl-lead with silver nitrate at very low temperatures yields a relatively unstable isobutenyl derivative of silver. At temperatures above −20 °C isobutene is formed preferentially together with a small amount of 2,5-dimethylhexa-2,4-diene (10%).[70] The detection of the olefin among the reaction products undoubtedly demonstrates the formation of free radicals in the decomposition of the corresponding silver compound. The author[70] proposed the following chain mechanism of the process with participation of the ethoxy-radical:

$$Et_3PbCH{=}CMe_2 \xrightarrow{AgX} Me_2C{=}CHAg \quad ,$$

$$Me_2C{=}CHAg \rightarrow Me_2C{=}CH^{\cdot} + Ag \quad ,$$

$$2Me_2C{=}CH^{\cdot} \rightarrow Me_2C{=}CH{-}CH{=}CMe_2 \quad ,$$

$$Me_2C{=}CH^{\cdot} + EtOH \rightarrow Me_2C{=}CH_2 + EtO^{\cdot} \quad ,$$

$$Et_3PbCH{=}CMe_2 + EtO^{\cdot} \rightarrow Et_3PbOEt + Me_2C{=}CH^{\cdot} \quad .$$

An analogous mechanism has been proposed for the reaction of tetravinyl-lead with silver nitrate[71§]. The hypothesis of the radical chain mechanism is based on the finding that, with decrease of the concentration of $AgNO_3$, the yield of isobutene increases[70]. However, Tamura and Kochi[79] showed that the metallic silver formed in the decomposition process can be oxidised by the nitrate ion and the effect of the $AgNO_3$ concentration observed by Glockling[70] might be partly due to this reaction. Thus the decomposition of vinylsilver is a radical process.

On the other hand, the tributylphosphine complexes of 1-propenyl- and 2-butenyl-silver decompose via the bimolecular mechanism, judging from stereochemical data, since the only reaction product, resulting from the coupling of the radicals, is formed with retention of the configuration of the sp^2-hybridised carbon atom[82].

We shall consider the decomposition reactions of aromatic derivatives of silver primarily in order to demonstrate the possibility of the occurrence of the radical and bimolecular mechanisms for this class of compounds and to discuss certain problems concerning the nature of the bimolecular mechanism.

It has been shown that in the joint decomposition of phenyl- and tolyl-silver in pyridine at 50–80 °C, the cross-coupling product is formed in a statistical proportion and that the addition of quinone diminishes appreciably the yield of not only ArH but also Ar_2.[75] There is no doubt that the decomposition of ArHg results in the formation of free radicals in this instance, apparently owing to the high reaction temperature.

In contrast to this, the reaction of silver bromide with a mixture of phenyl- and anisyl-magnesium bromides in ether leads to proportions of products which differ from the statistical distribution[83]:

$$\underset{}{PhMgBr} + \underset{}{p\text{-}MeOC_6H_4MgBr} \xrightarrow{AgBr} \underset{22\%}{Ph_2} + \underset{18.2\%}{PhC_6H_4OMe} + \underset{4.7\%}{(MeOC_6H_4)_2} \quad .$$

Furthermore, the relative yields of products depend on the concentration of the Grignard reagent. The authors[83] believe that ArAg decomposes via a radical pathway, but we think that the data presented actually support the bimolecular reaction mechanism.

The reactions of silver nitrate with tetraphenyl derivatives of tin and lead merit special attention[73]. Whereas in the first reaction the main product is benzene (80.6%) with only 5.2% of biphenyl, in the second case the main product is biphenyl (70.2%) and only trace amounts of benzene are produced. The observed differences between the compositions of the reaction products are undoubtedly associated with the different conditions in the decomposition of phenylsilver. Presumably the steady-state concentration of phenylsilver in the reaction of Ph_4Pb, which is much faster than the reaction of Ph_4Sn,[73] is high and the bimolecular decomposition of PhAg is therefore more probable. On the other hand, in the reaction of Ph_4Sn with $AgNO_3$ phenylsilver decomposes mainly via a radical mechanism and benzene is formed¶.

We believe that benzene can be formed also as a result of the catalytic decomposition of PhAg by silver nitrate. This view is confirmed indirectly by the finding that the complex

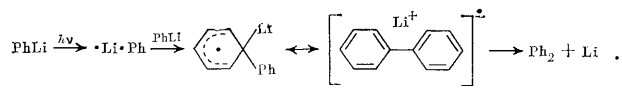
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§ A radical chain mechanism has also been proposed for the decomposition of RMe_2SiCH_2Ag (R = Me or Ph).[81]

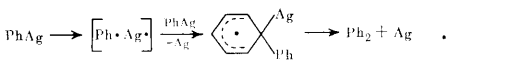
¶ The formation of benzene in this reaction can hardly be attributed to the radical chain mechanism considered above for vinyl derivatives of lead, because organotin compounds show a smaller tendency, compared with lead compounds, to enter into S_H2 reactions[84].

$5PhAg.2AgNO_3$ decomposes rapidly at room temperature, while pure phenylsilver is stable even in the course of a whole day[85]. Generally speaking, this is by no means a common phenomenon where the metal salt initiates the decomposition of an organic derivative of the same metal, particularly when the latter is in the same oxidation state. An attempt may be made to account for this finding by taking into account certain characteristics of silver compounds. The effect of silver nitrates in this reaction can be twofold: firstly, the Ag^+ cation is in principle capable of oxidising PhAg with formation of phenyl radicals, whereupon the reaction product is benzene, and, secondly, silver nitrate can prevent the formation of dimeric (polymeric) associated species, which are known for organosilver compounds[65]. We draw special attention to the possible role of the formation of associated species, because the latter can influence in a most unusual manner the pathway leading to the decomposition of organometallic compounds. On the other hand, the formation of associated species can increase the stability of the organosilver compound irrespective of decomposition. On the other hand, the decomposition of the associated species should lead to the formation of a dimer R_2, which is usually explained from the standpoint of the bimolecular mechanism.

Van Tamelen's mechanism, proposed for the photochemical decomposition of phenyl-lithium in ether[86], can involve an unusual mode of bimolecular decomposition of PhAg:

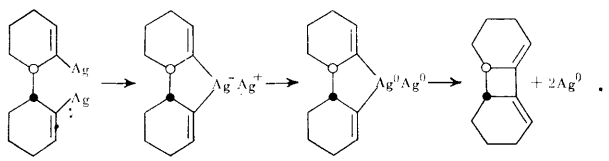


At first sight this photochemical reaction has little in common with the decomposition of PhAg, but these processes have the common feature that free radicals are not formed and the only product is biphenyl. By analogy with van Tamelen's mechanism, one can put forward the following mechanism for the decomposition of phenylsilver:



Evidently the formation of dimers can favour this course of reaction.

Another model for the decomposition of organosilver compounds without the involvement of free radicals has been considered by Moore et al.[87] These workers suggested that the intramolecular coupling products are formed in the decomposition of *d,l*-2,2′-disilver-3,3-bicyclohexenyl as a result of the following oxidation-reduction processes†:



In essence, this mechanism postulates the formation of intermediates whose structure is analogous to that of the organic cuprates R_2CuLi.

In conclusion of this section on the action of silver salts on organometallic compounds we may note that certain organic derivatives of non-metallic elements, for example, boron[88,89], react analogously. The reaction yields the corresponding silver compounds whose decomposition leads to the formation of coupling products.

Gold(I) salts have analogous chemical properties to those of silver salts; for example, their reaction with organoboron compounds results in the formation of the dimerisation products R_2 [89,90]

2. Reactions of Organometallic Compounds with Copper Salts

The reactions of organometallic compounds of the type RM with copper salts are undoubtedly more common and have been more thoroughly investigated than the reactions with silver salts. This is not surprising bearing in mind not only the wide variety of the products formed but also the definite synthetic value of these reactions. Depending on the oxidation state of copper, the hydrocarbon R_2 or RH and R(-H), as well as two-electron oxidation products, for example, organic halides in reactions with copper(II) halides, can be formed.

Leaving aside for the moment the details of the mechanisms of the interaction of organometallic compounds with copper salts, we may note that all these reactions usually proceed via a transmetallation stage. However, the intermediates formed are relatively stable only in the case of copper(I) compounds and they can be sometimes actually isolated at the usual temperature[85,91,92]. On the other hand, if the intermediates are very unstable, and this happens much more frequently, then their formation can sometimes be confirmed indirectly[93]. For example, Clinton and Kochi[94] established that the acetolysis of tetraethyl-lead is catalysed by copper(I) salts. The study of this phenomenon in a deuterated solvent showed that the kinetic isotope effect (KIE) in the reaction differs from that in the non-catalysed reaction (in the absence of copper salts, ethane-d_1 is formed six times more slowly than in the catalysed reaction). The results demonstrate convincingly the intermediate formation in the catalysed reaction of ethylcopper, which undergoes protolysis.

The oxidation of organometallic compounds by copper(II) salts proceeds similarly via a transmetallation stage. Although the corresponding intermediates have never been obtained, this view has now become firmly established. The mechanism of oxidation via a one-electron transfer stage appears unlikely in view of the low oxidising capacity of copper(II) salts[95] (admittedly the oxidation of carbanions may prove to be an exception to this rule). This can be illustrated fairly clearly by comparing the reactions involving the oxidation of tetraalkyl-lead by copper(II) chloride and the anion $IrCl_6^{2-}$, which is a one-electron oxidant:

$$R_4Pb + 2CuCl_2 \rightarrow RCl + R_3PbCl + 2CuCl \quad ,$$

$$R_4Pb + 2IrCl_6^{2-} \rightarrow RCl + R_3PbCl + 2IrCl_5^{2-} \quad .$$

The same product, namely alkyl chloride, is formed in both processes but there are significant differences between the reaction kinetics[96,97]. Whereas in the oxidation of tetraethyl-lead by $IrCl_6^{2-}$ the rate of reaction exceeds by a factor greater than 1000 the rate of oxidation of Me_4Pb, the opposite relation is observed in the reaction with $CuCl_2$—Me_4Pb proved to be 44 times more active than Et_4Pb. There is no doubt that these differences are due to the high steric hindrance by the bulky Et_3Pb group in the transmetallation reaction. Furthermore, in the oxidation of a mixed compound of the type $Et_{4-n}Me_nPb$ (n = 1–3) by $IrCl_6^{2-}$, the ethyl group shows a greater tendency to be split off, and not the methyl group as usually happens in electrophilic substitution.

† The open and filled circles denote carbon atoms having different configurations.

Combined analysis of the results of studies of the reactions of copper salts with organometallic compounds permits the differentiation of three main problems: (1) the mechanism of the formation and decomposition of organic derivatives of copper(I); (2) the mechanism of the reaction of organometallic compounds with copper(II) salts; (3) the possible pathways leads to the formation of the products of the two-electron oxidation of organometallic compounds by copper salts. All these problems are considered in subsequent sections.

3. Thermal Decomposition of Organocopper Compounds

Numerous studies on the thermal decomposition of organocopper compounds have been published recently. In these reactions the organic derivatives of copper(I) partly resemble the organosilver compounds, although, depending on the nature of the organic group in the RCu or RAg molecules and the reaction conditions, certain differences are also observed. Thus, in the thermal decomposition of alkylcopper, alkanes and alkenes are formed in maximum amounts rather than the coupling products R_2 as was the case for the silver compound. Alkanes and alkenes are virtually the only decomposition products of alkylcopper stabilised by trialkylphosphines and their ratio may be the same[30]. For example, butane and but-1-ene in proportions of 49 : 51, hydrogen (10%), and less than 0.1% of octane are formed in the thermal decomposition of the tributylphosphine complexes of butylcopper in ether[21,82]. The decomposition of 5-hexenylcopper-(I) in a complex with tributylphosphine in ether gives rise to 44% of hex-1-ene, 52% of hexa-1,5-diene, and only 3.5% of cyclic hydrocarbons[81]. In this case the reaction does not have a radical mechanism, since it is known that the cyclisation of hexenyl radicals is faster than the abstraction of hydrogen from the solvent[98,99]. Furthermore, it has been shown that the rate of decomposition of alkylcopper is not influenced by the addition of "radical trapping agents" such as styrene[21,82,100,101]. To explain the results, a mechanism has been proposed for the thermal decomposition with participation of copper hydride[21,100]:

$$\text{a. } \mathrm{BuCu \cdot P(n\text{-}Bu)_3} + \mathrm{CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2} \rightarrow \mathrm{HCu \cdot P(n\text{-}Bu)_3} + \text{cyclic hydrocarbons},$$

$$\text{b. } \mathrm{BuCu \cdot P(n\text{-}Bu)_3} + \mathrm{HCu \cdot P(n\text{-}Bu)_3} \rightarrow \mathrm{BuH} + 2\mathrm{Cu} + 2\mathrm{P(n\text{-}Bu)_3}.$$

Analysis of the products formed in the decomposition of a mixture of RCu and R'Cu (R = Et, and R' = Pr or iso-Pr) showed that there are two independent decomposition pathways:

$$\mathrm{EtCu + PrCu \text{ or iso-PrCu} \rightarrow} \begin{cases} \xrightarrow{a} \mathrm{C_2H_6 + C_3H_6 + 2Cu}, \\ \xrightarrow{b} \mathrm{C_2H_4 + C_3H_8 + 2Cu}. \end{cases}$$

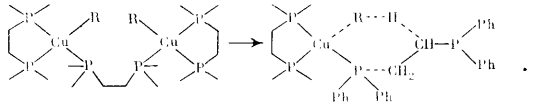
Pathway *a* proves to be dominant in the case of PrCu, while pathway *b* is dominant for iso-PrCu, which has been explained[78] by the easier reduction of secondary derivatives by copper hydride compared with the primary derivatives.

There exists the view that copper hydride is formed in the thermal decomposition of alkylcopper as a result of the β-elimination of the hydride ion[21], similarly to the formation of hydrides of other transition metals on decomposition of unstable organometallic compounds[102]. However, it is difficult to explain from this standpoint why the olefin is formed mainly from the ethyl fragment in the decomposition of a mixture of ethylcopper and isopropylcopper[78], since the hydride ion is usually abstracted from the carbon atom with the smallest number of hydrogen atoms. We believe that the thermal decomposition reactions are in reality of the radical type but occur within the complex. In fact, if the decomposition takes place within a binuclear complex formed in the solution, for example, on elimination of a phosphine ligand, then the heterolysis of the C–C bond will occur more readily in the case of isopropylcopper; in its turn the radical formed abstracts a β-hydrogen from another organic group#.

One may point to a certain analogy between the reaction mechanism discussed above and the mechanism proposed by Miyashita and Yamamoto[104], who investigated the thermal decomposition of the 1,2-bis(diphenylphosphino)ethane complex of RCu (R = Me, Et, Pr, or iso-Bu). It was found that this reaction does not proceed entirely in the usual manner—biphenylvinylphosphine is formed together with an alkane:

$$(\mathrm{RCu})_2(\mathrm{dppe})_3 \xrightarrow{\mathrm{THF}} \mathrm{Ph_2PCu(dppe)} + \mathrm{RH} + \mathrm{Ph_2PCH{=}CH_2} + \mathrm{RCu(dppe)};$$
$$\mathrm{dppe} = \mathrm{Ph_2PCH_2CH_2PPh_2}.$$

The authors[104] believe that an intramolecular reaction with a phosphine ligand in which there is a concerted transfer of hydrogen and the cleavage of a carbon–phosphorus bond, takes place in this instance:



An interesting feature of the decomposition reaction of alkylcopper and possibly of other copper(I) derivatives is that the process can be catalysed by metals and not only by copper and silver but also by palladium[100]. Thus the decomposition of alkylcopper is an autocatalytic process and the induction period observed in this reaction diminishes following the addition of metals which can be arranged in the following sequence in terms of their activities: Cu > Ag > Pd. The formation of the paramagnetic dinuclear organocopper intermediate $[\mathrm{EtCu^I.Cu^0}]$ was demonstrated by EPR in the decomposition of ethylcopper in THF. The authors[100] proposed the following mechanism of the catalytic process involving the species:

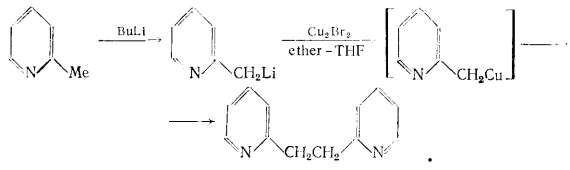
$$\mathrm{RCu^I + Cu^0} \rightarrow [\mathrm{RCu^ICu^0}],$$

$$[\mathrm{RCu^ICu^0}] \xrightarrow{\text{fast}} \mathrm{R(-H) + Cu^0 + CuH},$$

$$\mathrm{RCu^I + CuH} \rightarrow \mathrm{RH + 2Cu^0 \text{ etc.}}$$

However, we believe that the catalytic decomposition of alkylcopper can also occur on the surface of the metal. The copper atoms formed in the reaction are incorporated in the metal lattice and the resulting energy gain, equal to the heat of condensation, is the decisive factor in this catalytic reaction.

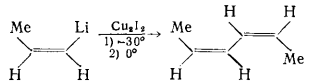
Benzyl derivatives of copper(I) are particularly unstable and readily decompose during preparation with formation of the dimer R_2. This reaction is used, for example, in the dehydrodimerisation of picolines[105,106]:



Since benzyl radicals usually dimerise and do not abstract hydrogen from the solvent, the formation of R_2 in the decomposition of benzyl derivatives of copper(I) is no longer a criterion of a bimolecular reaction mechanism. The homolytic dissociation of a carbon–metal bond can occur in this reaction with equal success.

The radical abstraction of a β-hydrogen atom is known to occur, for example, in the reaction of organomercury compounds with $CCl_3^{\cdot}$.[103]

Dienes are formed in the decomposition of vinyl derivatives of copper as in the case of silver compounds. The reaction is more stereospecific both in the presence and in the absence of tributylphosphine[23,82,107]. This is usually regarded as an argument against a radical reaction pathway:



Judging from the formation of the hydrocarbon ArH, the decomposition of the aryl derivatives of copper ArCu takes place in many instances via a radical mechanism[75]. The thermal decomposition of 2-dimethylaminophenylcopper in dimethylformamide (DMF) apparently takes place in this way, since *N*,*N*-dimethylaniline is formed in this reaction together with 2,2′-bis(dimethylamino)diphenyl (40%).[108] Even in the complex with 1,2-bis(diphenylphosphino)ethane this compound decomposes with participation of radicals and diphenylvinylphosphine is formed in addition to *N*,*N*-dimethylaniline [109] (see the analogous reaction for alkyl compounds of copper[104]).

At the same time there exist data showing that aryl derivatives of copper(I) can decompose without the participation of free radicals[111,112]. This applies particularly to the decomposition of various cluster compounds. Thus the decomposition of the octanuclear cluster $(m\text{-}CF_3C_6H_4)_8Cu_8$ yields biaryl and a cluster assumed to be of the type R_4Cu_8.[113,114] However, this cluster apparently decomposes via a radical mechanism, since trifluoromethylbenzene is then formed[114].

The dimer 2,2′-bis(dimethylamino)biphenyl is formed in a yield exceeding 90% on decomposition of $(2\text{-}Me_2NC_6H_4)_4Cu_6Cl_2$, while the decomposition of the corresponding non-cluster compound yields mainly *N*,*N*-dimethylaniline[108]. The steric proximity of the aryl group in this hexanuclear cluster promotes this reaction pathway[115]. The relative positions of the groups Ar and R (Ar = $2\text{-}Me_2NC_6H_4$, R = PhC≡C) determine similarly the decomposition of the cluster $Ar_4R_2Cu_6$. The only product of this reaction is ArR and there are not even traces of R_2 and Ar_2.[116,117]

The data presented show that the formation of cluster intermediates is important for the decomposition of organocopper compounds with formation of radical coupling products. The finding that the yield of 1-phenyl-1-propyne reaches 75% in the joint decomposition of methyl- and phenylethyl-copper in ether[118], i.e. greatly exceeds the yield expected for statistical coupling of the radicals, can be explained from this standpoint[1].

IV. THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS OF OTHER METALS

To complete the overall picture of the state of research into the thermal decomposition of organic derivatives of metals, particularly those of the copper subgroup, we shall consider data for the decomposition of compounds of other transition metals. The decomposition of alkylgold(I) stabilised by triphenylphosphine, in both the solid phase and in solution in decalin at a temperature close to 100 °C, leads to the formation of products of the radical dimerisation and disproportionation reactions[119]. Thus ethane and a very small amount of methane are formed from methylgold, butane (90%), ethane (1.4%), and ethylene (0.7%) are formed from ethylgold, propane (28%), propene (34%), and only traces of 2,3-dimethylbutane are formed from isopropylgold, while t-butylgold gives rise to isobutane (13%), isobutene (48%), and a certain amount of unidentified products.

Thus it can be seen that the thermal decomposition reactions of primary derivatives of alkylgold resemble those of the silver derivatives, while the reactions of the secondary and tertiary derivatives take place analogously to the decomposition of the copper compounds. The study of the kinetics of the decomposition of the triphenylphosphine complex of methylgold in decalin showed that the reaction is of first order with respect to $MeAu.PPh_3$. This suggested that the rate-determining stage is the elimination of the triphenylphosphine ligand:

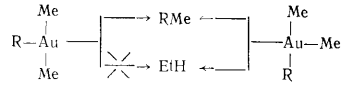
$$MeAu \cdot L \xrightarrow{k_1} MeAu + L \ ,$$
$$MeAu \cdot L + MeAu \rightarrow EtH + 2Au + L \ .$$

In contrast to alkyl derivatives of gold(I), the thermal decomposition of trialkylgold takes place as reductive elimination[120,121], for which various mechanisms have been proposed depending on the nature of the solvent:

$$Me_3AuL \rightarrow EtH + MeAuL \ .$$

The study of the products of the thermolysis of equimolar mixtures of Me_3AuPPh_3 and $(CD_3)_3AuPPh_3$ showed that at 80 °C in decalin and chlorobenzene the decomposition reaction is unimolecular, because a statistical average distribution of products is obtained ($C_2H_6 : CH_3CD_3 : C_2D_6 = 1 : 2 : 1$). On the other hand, in polar solvents [dimethyl sulphoxide (DMSO) and DMF] at a low concentration of trialkylgold the reaction proceeds almost exclusively via an intramolecular mechanism and the yield of the cross-coupling product reaches only 5% in this instance. The results of the study of the decomposition reaction of $CD_3Me_2AuPPh_3$ also agree with this conclusion; in chlorobenzene the yields of EtH, $MeCD_3$, and C_2D_6 are in the proportions 49 : 46 : 6, while in DMSO these ratios are 25 : 75 : 0.

It has been shown for *cis*- and *trans*-RMe_2AuPPh_3 (R = Et or Pr)[121] that the yield of ethane in the decomposition of the *cis*-isomer in decalin greatly exceeds that in the case of the *trans*-isomer, which agrees with an intramolecular process occurring as stereospecific *cis*-elimination:



In contrast to this, in the decomposition of *cis*- and *trans*-$CD_3Me_2AuPPh_3$ in decalin, the composition of the products is independent of the isomer undergoing decomposition which indicates the intermolecular nature of the reaction. Thus the mechanism of the thermal decomposition of trialkylgold is largely determined by the nature of not only the solvent but also of the alkyl group.

The phosphine complexes of dialkylgold salts decompose similarly—via intermolecular reductive elimination[122]:

$$[R_2Au(PPh_3)_2]O_3SCF_3 \rightarrow R_2 + Au(PPh_3)_2O_3SCF_3 \ ,$$
$$R = Me, Et, Bu \ .$$

A characteristic feature of the majority of the thermal decomposition reactions of organometallic compounds of transition metals is inhibition of the process following the addition of complex-forming agents. For example, it is known that alkylcopper is absolutely unstable at room temperature, while some of its phosphine complexes are fairly stable under these conditions[104]. The rate of the decomposition reaction of phosphine complexes of trialkylgold[121] and salts of dialkylgold[122] examined above diminishes appreciably after the addition of substituted phosphines. An analogous effect of added phosphines is manifested in the reductive

elimination of triethylphosphine complexes of methylarylnickel:[123]

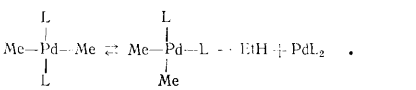
$$(Et_3P)_2NiArMe \rightarrow ArMe + (Et_3P)_2Ni \quad .$$

It is usually assumed that the addition of complex-forming agents prevents the formation of coordination-unsaturated intermediates, while the electronic structure favours the decomposition reaction. This has been confirmed, for example, in a thermographic study[124] of the decomposition of the complexes C_6F_5CoL (L = Schiff base) with various ligands Q (Q = H_2O, NH_3, Py, etc.). It was shown that the formation of perfluorobiphenyl in this reaction is always preceded by the ligand elimination stage, i.e. the process takes place in stages:

$$RCoLQ \rightarrow RCoL + Q \quad ,$$
$$RCoL \rightarrow CoL + 1/2R_2 \quad .$$

For some ligands, the elimination of Q takes place at temperatures lower than that required for further decomposition of RCoL. Other ligands are so strongly coordinated to the metal atom that their elimination requires a higher temperature at which both reactions—the elimination of Q and the formation of R_2—take place simultaneously.

Another explanation of the influence of added ligands on the decomposition of metal complexes has been given in a study[125] of the intramolecular decomposition of phosphine complexes of dimethylpalladium leading to the formation of ethane. It was found that this reaction occurs only for *cis*-complexes, while the decomposition of *trans*-complexes proceeds via the *trans–cis* isomerisation stage. The latter process is facilitated in the presence of polar solvents and added ligands:



Thus the influence of added ligands on the decomposition of metal complexes may be associated with the acceleration of the *trans–cis* isomerisation and also with the increase of the concentration of active species having the *cis*-configuration.

However, processes are known in which added complex-forming agents facilitate the thermal decomposition of complexes already having the *cis*-configuration. Thus the intramolecular reductive elimination reaction of *cis*-$PtAr_2L_2$ in toluene at 60 °C is accelerated in the presence of free triarylphosphine[126]:

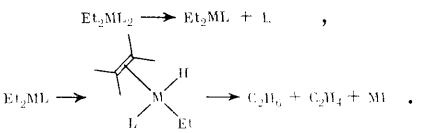
$$PtAr_2L_2 \rightarrow Ar_2 + PtL_2 \quad ,$$
Ar = Ph, p-MeC_6H_4; L = PPh_3, (p-$MeC_6H_4)_3P$.

The kinetics of this reaction have been studied in very great detail, but the mechanism of the influence of triphenylphosphine on the rate of the process remains unelucidated.

We shall consider a further two types of thermal decomposition reactions of organic compounds of transition metals. One of these consists of reductive elimination reactions leading to the formation of alkanes and alkenes, an example of which is provided by the decomposition of dialkyl complexes of cobalt(III),[127] palladium(II),[128] platinum(II),[129] and iron(II):[130,131]

$$MR_2L_n \rightarrow RH + R(-H) + ML_n \quad .$$

Studies of the kinetics of the decomposition of $CoR_2(acac).(PR'_3)_2$,[127] $Et_2Pd(PR'_3)_2$,[128] and $Et_2Pt(PEt_3)_2$ [129] showed that the reactions are of first kinetic order, i.e. are intramolecular. On the basis of these results as well as data for the influence of the nature of the group R on the thermal stability of organometallic compounds, a reaction mechanism has been proposed, according to which the decomposition of the compounds is preceded by the ligand displacement stage and the formation of a metal hydride complex:



Judging from the values of the kinetic isotope effect in the reactions of R_2ML_n with R = Et and CD_3CH_2, any of these stages can be the rate-determining step[129].

Another reaction which has attracted the attention of investigators recently is the thermal decomposition of organometallic compounds involving the transfer of an α-hydrogen atom[132,133]. It was shown, for example, that the decomposition of pentabenzyltantalum proceeds precisely in this manner[134]:

$$(PhCH_2)_5Ta \rightarrow PhCH_3 + (PhCH{=})_5Ta_2 \quad .$$

This reaction is apparently intramolecular and takes place without the formation of free radicals, because α-deuterotoluene is not formed when the decomposition of $(PhCH_2)_5Ta$ is carried out in C_6D_6 and the reaction is not accelerated in the presence of radical initiators.

V. ONE-ELECTRON OXIDATION OF ORGANOMETALLIC COMPOUNDS BY COPPER(II) SALTS

The mechanism of the reactions of organometallic compounds with copper(II) salts differs significantly from the mechanism of the reactions with copper(I) salts. Bawn and Whitby[76] investigated the reaction of tetramethyl-lead with coppper(II) nitrate in ethanol and showed that it results in the formation of ethane and methane in proportions of 1 : 0.47. They put forward the hypothesis that the reaction proceeds in stages. The first stage is of the oxidation-reduction type and leads to the formation of radicals and a copper(I) salt:

$$Cu^{2+} + Me_4Pb \rightarrow Cu^+ + Me_3Pb^+ + Me^\cdot \quad ,$$
$$2Me^\cdot \rightarrow EtH \quad .$$

In the second stage the interaction of $(CH_3)_4Pb$ with Cu^+ leads to the formation of an organocopper compound which undergoes thermal decomposition:

$$Cu^+ + Me_4Pb \rightarrow MeCu + Me_3Pb^+ \quad ,$$
$$MeCu \xrightarrow{EtOH} MeH + Cu^0 \quad .$$

An analogous reaction mechanism was subsequently examined for the interaction of organolithium compounds with copper(II) chloride[135].

Despite the fact that subsequent studies showed that the mechanism of Bawn and Whitby is largely correct, in its initial version[76], proposed for the methyl system, there was a clear contradiction. In fact, in the first stage of this mechanism[76] methyl radicals dimerise, while in the second stage they abstract hydrogen from the solvent (although it would seem that this process should be the only one occurring if the reaction does indeed involve the formation of free methyl radicals). Furthermore, it is known that the decomposition of alkyl derivatives of copper(I), even those containing a β-hydrogen atom, results in the formation of a considerable amount of a radical coupling product (see Section III), whereas according to the mechanism of Bawn and Whitby only methane is obtained at this stage.

Studies[136,137] which established that the butane formed in the reaction of tetraethyl-lead with copper(II) nitrate is obtained on decomposition of ethylcopper are remarkable in

this connection. This conclusion is based on the finding that butane is not formed in the presence of *p*-dimethylaminobenzylidenerhodanine (A) [which forms complexes with copper(I) salts], while in the absence of the rhodanine its yield is 17%:

$$Et_4Pb \xrightarrow{Cu(NO_3)_2} EtH + C_2H_4 + BuH + Et_3PbNO_3 + Cu^0$$

	EtH	C_2H_4	BuH
In the absence of A	77%	6%	17%
In the presence of A	86%	14%	0%

Furthermore, it has been shown in special experiments that[136,137] the decomposition of ethylcopper leads to the formation of butane:

$$\underset{74\%}{EtCu} \rightarrow \underset{74\%}{EtH} + \underset{0\%}{C_2H_4} + \underset{26\%}{BuH} + Cu^0 \quad .$$

The data presented are also of interest from the point of view that they demonstrate the formation of ethylcopper only as a result of the reaction of the initial organometallic compound with copper(I) nitrate. This makes it possible to reject the mechanism of Thiele and Kohler[138], who believe that the reactions of organometallic compounds with copper(II) salts proceed via a stage involving the total transmetallation and subsequent decomposition of the copper(II) derivative[138]:

$$Alk_2Zn + CuCl_2 \rightarrow ZnCl_2 + Alk_2Cu \quad ,$$
$$Alk_2Cu \rightarrow AlkCu + Alk^{\cdot} \quad .$$

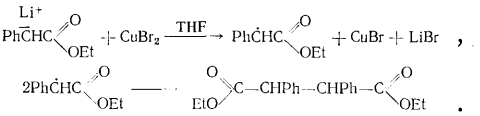
This mechanism is unlikely also because it is difficult to imagine the formation of dialkylcopper by-passing the stage involving the formation of a mixed derivative RCuX. If the latter compound had in fact been obtained, then, by virtue of its instability, it would have decomposed before being able to react with another molecule of dialkylzinc. However, its decomposition should occur with the cleavage of the R–Cu bond, in contrast to dialkylcopper, and cannot lead to the formation of alkylcopper:

$$RCuX \rightarrow R^{\cdot} + CuX \quad .$$

Thus the main feature distinguishing the mechanism of the interaction of organometallic compounds with copper(II) salts is the formation of free radicals. Their generation in these reactions was demonstrated by introducing "radical trapping agents" such as diphenylpicrylhydrazyl[136] or by initiating the polymerisation of monomers added to the reaction mixture[76,136]. In all cases the yield of the products of the radical reactions, mainly alkanes, diminished under these conditions.

The formation of free radicals is also indicated by the nature of the products obtained. Thus, when triethylaluminium is refluxed with copper(I) and copper(II) chlorides in cyclohexane, ethane and ethylene are formed in proportions of ~2 : 1 together with a small amount of butane (2–9%).[27] The composition of the mixture of products depends little on the oxidation state of copper in the salt used. In the reaction of organolead compounds of the type of R_4Pb with copper(II) salts, several products are formed whose ratio depends on the nature of R and X. Thus the interaction of tetraphenyl-lead or tetraphenyltin with copper(II) nitrate in ethanol results in the quantitative formation of benzene[73], tetramethyl-lead gives rise to methane (21.2%) together with ethane (74.6%),[73,135] while the reaction of tetraethyl-lead leads to the formation of ethane, ethylene, and butane in the same proportions as in the reaction with silver nitrate (26.3% EtH, 16.7% C_2H_4, and 52.5% BuH).[73,76,136]

At the same time reactions of organometallic compounds are known in which the yield of radical coupling products is greater—for example, the oxidation of the lithium enolates of acetate esters, acetic acid derivatives[139], and ketones[140]. These reactions are usually regarded as electron transfer from the enolate to the copper(II) halide with subsequent dimerisation of the radicals:



The coupling of radicals in reactions of diphenylmethyl[141,142] and fluorenyl derivatives of lithium[142] with copper(II) halides apparently proceeds analogously. This pathway most probably operates when fairly stable radicals are formed in the reaction. For the usual reactions of organometallic compounds, a hypothetical mechanism postulating the involvement of organic copper(II) chlorocuprates of the type $[RCuCl_3]^{2-}$ in the coupling reaction has been proposed[20].

Organic compounds of copper(II) are known to be exceptionally unstable; any attempt to prepare them led to the formation of radicals. On the other hand, one cannot rule out the possibility of an increase of the stability of RCuCl as a result of coordination to ligands, for example, the chloride ion. The number of examples of such stabilisation of organometallic compounds is fairly large; it is sufficient to mention that the majority of σ-linked transition metal compounds are stable by virtue of such coordination. The existence of copper(I) cuprates of the type of R_2CuM, widely used in organic synthesis[64], has also played a considerable role in the development of ideas about the organic copper(II) chlorocuprates.

The mechanism of the coupling of organometallic compounds with participation of chlorocuprates has been invoked to account for the results of the study of the reaction of RMgBr with Li_2CuCl_4 in THF.[20] Its products are the dimers R_2 and organic chloro-derivatives RCl; the products do not contain the hydrocarbons RH. The ratio of R_2 and RCl depends on the reactant concentrations and the yield of the dimeric products increases with increasing RMgBr concentration.

[EtMgBr]/[Cu^{2+}]	BuH, %	EtCl, %
0.6	50.6	49.4
1.2	53.9	46.1
2.9	73.7	26.3

The yield and proportions of the products are not influenced by the addition of styrene, which rules out the possibility of the formation of free radicals in this reaction. The authors[20] proposed the following reaction scheme, in which organic chlorocuprates decompose via a bimolecular mechanism with formation of a dimeric product:

$$(Cu^{II}Cl_4)^{2-} + RMgBr \rightarrow [RCuCl_3]^{2-} + MgBrCl \quad ,$$
$$2\,[RCuCl_3]^{2-} \rightarrow R_2 + 2\,(Cu^{I}Cl_2)^{-} + 2Cl^{-} \quad .$$

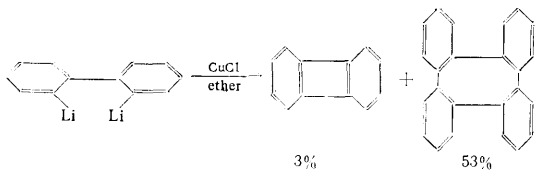
Yet another possibility of the formation of coupling products in these reactions should be noted. According to Whitesides et al.[143], treatment of the homocuprate Bu_2CuLi in THF with the copper(II) chloride complex of tetramethylethylenediamine (TMEDA) leads to the formation of octane:

$$Bu_2CuLi \xrightarrow[THF]{CuCl_2 \cdot TMEDA} Bu{-}Bu \quad .$$

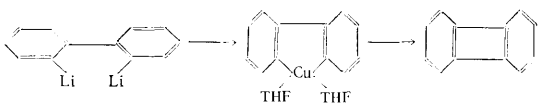
One cannot therefore rule out the possibility that organic cuprates, whose subsequent oxidation leads to the formation of dimeric products, are formed in the reactions of organic compounds of lithium and possibly also magnesium with copper(II) salts.

The involvement of cuprates can be postulated in the reaction of 2,2′-dilithiobiphenyl with copper(II) chloride in ether[64], while diphenylene and tetraphenylene are formed

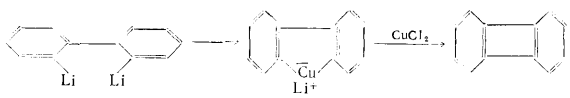
together with biphenyl and *o*-quaterphenyl:[14,144-146]



When a 1 : 1 mixture of ether and THF is used as the solvent, the yield of diphenylene increases to 36% and that of tetraphenylene falls to 24%. According to the authors[146], THF stabilises the intermediate R_2Cu, which increases the contribution of the decomposition via the intramolecular mechanism:



However, it is most likely that cuprates are formed, whose oxidation leads to intramolecular coupling:



The formation of the remaining products—tetraphenylene and *o*-quaterphenyl—can be account for analogously.

In our view, cuprates can also be involved in the reactions of vinyl derivatives of aluminium with copper(II) chlorides, because dienes are formed in this reaction with retention of the configuration at the carbon atom[147]. If free vinyl radicals participated in the reaction, the geometrical configuration might be distorted somewhat, but in the first place this would involve the abstraction of hydrogen from the solvent molecule with formation of an olefin.

There exists yet another possibility of the formation of coupling products in the oxidation of organometallic compounds by a copper(II) salt. It is known that organic copper(I) compounds, formed in these reactions as intermediates, give rise to associated species having the polymeric 3*c*–2*e* structure. This specific feature of the structure of the organometallic compounds can favour the formation of the dimers R_2 in the subsequent oxidation reaction[1]. This applies particularly to the oxidation of ethynyl derivatives of metals in which copper acetylides, existing only in a polymeric form, are formed. For example, in the interaction of copper(II) halides with ethynyl Grignard reagents[148] or with the corresponding derivatives of gold, silver, and copper[149,150], the yield of the dimeric product is as a rule quantitative:

$$RC{\equiv}CM + CuCl_2 \xrightarrow[M=Cu,\ Ag,\ Au]{THF} RC{\equiv}C{-}C{\equiv}CR + CuCl + MCl \ .$$

Another product of the reactions of organometallic compounds with copper(II) halides is an organic halide. It is evidently the product of the two-electron oxidation of the organometallic compound, since a carbonium ion linked to a halide ion is then formed from the carbanion R^- in RM. There exist various views on the mechanism and the formation of such halides; the next section is devoted to the consideration of this question and in general to the two-electron oxidation of organometallic compounds.

VI. TWO-ELECTRON OXIDATION OF ORGANOMETALLIC COMPOUNDS

A greater number of possible mechanisms have been considered for the two-electron oxidation of organometallic compounds than for the one-electron oxidation. In principle, such oxidation can occur in stages as a result of the successive transfer of two electrons from the organic group R:

$$RMX_n \xrightarrow{-e^-} R^\cdot + MX_n^+ \ ,$$
$$R^\cdot \xrightarrow{-e^-} R^+ \xrightarrow{Nu^-} RNu \ .$$

However, it has been suggested for certain reactions that the conversion of RM into RNu takes place in a single stage via a heterolytic mechanism, which can be formally regarded as nucleophilic substitution:

$$RMX_n + Nu^- \longrightarrow RNu + MX_{n-1} + X^- \ .$$

The role of the transition metal salt in these processes can be most varied: it can participate in the transmetallation reaction, can manifest the properties of an oxidant, and can even catalyse the single-stage two-electron oxidation.

1. Oxidation by Bivalent Copper Salts

The two-electron oxidation takes place particularly frequently in the reactions of organometallic compounds with copper(II) salts, for example with copper(II) halides. It was shown in Section V that the primary product of these reactions may be free radicals and one can therefore suggest that these are in fact the species oxidised by the copper(II) salt with formation of the two-electron oxidation product RX:

$$RMX_n + CuX_2 \longrightarrow [RCuX] + MX_{n+1} \ ,$$
$$RCuX \longrightarrow R^\cdot + CuX \ ,$$
$$R^\cdot + CuX_2 \longrightarrow RX + CuX \ .$$

The studies by Kochi and coworkers[151-153], which established that the radicals are very effectively oxidised by copper(II) salts, greatly promoted the development of such ideas. It has been shown for alkyl radicals that their oxidation by copper(II) acetate leads to the formation of carbonium ions, which are stabilised either by eliminating a proton with formation of an olefin or by interacting with the solvent to form solvolytic products. The reaction with copper(II) chloride yields bromoalkanes, i.e. the radicals are oxidised with simultaneous "ligand transfer". It has been suggested that the oxidation of the radicals leads to the intermediate formation of an unstable copper(III) compound§, which is converted into RX by oxidative substitution[152]:

$$R^\cdot + CuX_2 \rightleftarrows [RCuX_2] \ ,$$
$$[RCuX_2] \rightleftarrows R^+CuX_2^- \rightarrow RX + CuX \ .$$

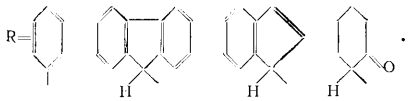
In agreement with these data, organic halides are formed in the reaction of organometallic compounds with copper(II) halides, while the reaction with copper acetate leads to acetates and olefins (in the case of alkyl derivatives of metals). For example, it has been frequently noted that the reaction of R_2Hg or RHgX (R = Ph, $PhCH_2$, ferrocenyl, etc.) with copper(II) halides results in the formation of halogenoderivatives RX or solvolytic products[33,35,156-165]. Using an excess of copper(II) bromide in dimethylformamide and most

§ The hypothesis of the intermediate formation of unstable copper(III) compounds has been recently confirmed in a study of the oxidation of radicals by a peptide complex of copper(II).[154]

varied radicals R [Bu, Ph, $PhCH_2$, C_6F_5, $C_6F_5CH_2$, $(CF_3)_2CH$, $PhCOCH_2$, CCl_3], it is possible to obtain organic bromides in nearly quantitative yields[160].

The interaction of organotin compounds $RSnMe_3$ with $CuBr_2$ in methylene chloride similarly results in the formation of the corresponding bromides RBr, whose yield is also quantitative [161]:

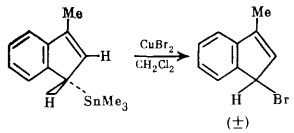
$$RSnMe_3 + 2CuBr_2 \rightarrow RBr + Me_3SnBr + 2CuBr ,$$

R=  .

This reaction is remarkable in the sense that with its aid organic bromides containing electron-accepting groups such as 9-fluorenyl, indenyl, and 2-cyclohexanonyl have been obtained. The point is that fairly stable free radicals are formed as intermediates in the oxidation of the corresponding organometallic compounds. In the case of more active derivatives of lithium or magnesium, radicals are not usually oxidised but dimerise, since the copper(II) halide reacts preferentially with the initial organometallic compound (see Section V). However, in the reactions of covalent derivatives of tin the radicals are oxidised to organic bromides.

It follows from the foregoing that both two-electron and one-electron oxidation is possible in the interaction of copper(II) salts with organic derivatives of metals RM and in general with organic derivatives of the elements, whose chemical properties are similar to those of organometallic compounds and the relative contributions of the two reaction pathways for derivatives of a single element depend on the nature of R and X in CuX_2. This can be seen in relation to the reactions of readily oxidised oxidisable organoboron compounds. Thus treatment of trialkylboranes[161] and phenylboronic[162], thienylboronic[163], ferrocenylboronic[164], and cymantrenylboronic acids[165] with copper(II) halides leads to the formation of organic halides only. In contrast to this, the interaction of organoboron compounds of copper(II) acetate usually results in the formation of one-electron oxidation products—the corresponding dimers[164-168]. The intermediate formation of an organic copper(I) compound, which decomposes in benzene with formation of R_2 and the product RH of the interaction of radicals with the solvent, was detected in the reaction of cymantrenylboronic acid[167]. The two-electron oxidation by copper(II) acetate is known for trialkylboranes, the products of the reactions of which are olefins[161], and for ferrocenylboronic acid, the oxidation of which gives a 59% yield of acetoxyferrocene[168].

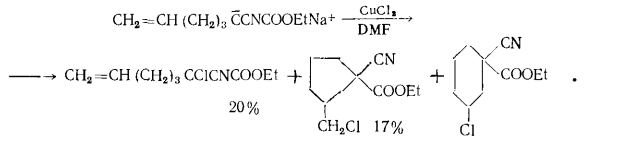
The involvement of free radicals in the reactions of organometallic compounds has not been confirmed solely by the formation of one-electron oxidation products, stereochemical evidence also being available. Thus the formation of free radicals in the reaction of $CuBr_2$ with alkyl derivatives of mercury has been demonstrated[169]. It was found that, regardless of which diastereoisomer of 3,3-dimethyl-1,2-dideuterobutylmercury chloride is introduced into the reaction, a mixture of deuterated neohexyl bromides with the same contents of the *threo*- and *erythro*-isomers is alway formed. The same stereochemical approach has been used to demonstrate the formation of radicals in the oxidation of organotin compounds—the racemic 1-bromo-3-methylindene was obtained in the reaction of the optically active *S*-(+)-3-methylindenyltrimethyltin with $CuBr_2$:[160]



(±)

There is no doubt that the loss of stereochemical configuration occurred in the indenyl radical formation stage.

The cyclisation of the hexenyl radical has been used as a test for its formation in reactions of the sodium enolate of the ethyl ester of 2-cyanohept-6-enoic acid with CuX_2 (X = Cl, SO_4, OAc, PhCOO, or p-$NO_2C_6H_4COO$) in DMF.[170] Derivatives of cyclopentane- and cyclohexane-carboxylic acids were detected in the reaction mixture:



The majority of investigators agree that the oxidation of organometallic compounds by copper(II) salts usually occurs with participation of free radicals, but it has been suggested that free radicals are not formed in some of the reactions. The reaction of Grignard reagents with the chlorocuprate Li_2CuCl_4 in THF, which has already been considered, apparently belongs to processes of this type[20]. Its products are the dimers R_2 and the chloro-derivatives RCl, which is obtained, according to the authors[20], in the oxidation of the intermediate organic chlorocuprate:

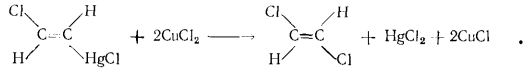
$$RMgBr + (CuCl_4)^{2-} \rightarrow [RCuCl_3]^{2-} + MgBrCl ,$$
$$[RCuCl_3]^{2-} + (CuCl_4)^{2-} \rightarrow RCl + 2(CuCl_2)^- + 2Cl^- .$$

The observed increase of the yield of RCl with increase of the Li_2CuCl_4 concentration agrees with this view. By analysing the overall kinetic reaction mechanism, it is possible to show that such dependence of the yield of RCl on the Li_2CuCl_4 concentration is possible only when RCl is obtained as a result of the oxidation of $[RCuCl_3]^{2-}$ and not of the radical R$^{\cdot}$ formed in the homolysis of this intermediate.

Kinetic analysis also leads to serious objections to the possibility of the formation of RCl as a result of the intramolecular decomposition of the intermediate RCuCl via the mechanism

$$RCu^{II}Cl \rightarrow RCl + Cu^0 .$$

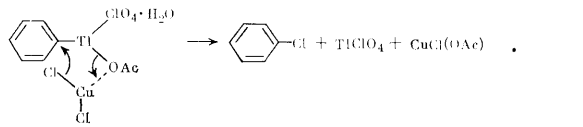
This pathway to the formation of two-electron products of organometallic compounds has been considered in a study[155] of the reaction of *trans*-β-chlorovinylmercury chloride with copper(II) chloride:



According to the authors[155], free radicals are not formed in this reaction, since it takes place with retention of the geometrical configuration at the carbon atom—*trans*-dichloroethylene is obtained from *trans*-β-chlorovinylmercury chloride, while *cis*-dichloroethylene is obtained from the *cis*-isomer[171]. However, this test for the formation of radicals is not very reliable, because it postulates that the loss of configuration in the vinyl radical occurs faster than its oxidation by copper(II) chloride. This cannot be claimed *a priori*, particularly if account is taken of the fact that the vinyl radicals invert much more slowly than alkyl radicals.

Finally, we shall consider the heterolytic mechanism of the two-electron oxidation of organometallic compounds by copper(II) halides which has been proposed for the oxidation of organic derivatives of thallium(III). According to this mechanism, the formation of organic halides proceeds in a

single step involving the elimination of thallium with reduction of thallium(III) to thallium(I), catalysed by the copper(II) salt[55,156,172]:



Formally this process can be regarded as substitution via the S_NC mechanism, but this is not the usual nucleophilic substitution because its driving force is the ability of thallium(III) to act as a two-electron oxidant. Furthermore, the role of the copper(II) salt in this mechanism is not clear.

One must note that the products of the one-electron oxidation ArH and Ar_2 are also formed in this reaction and the yields of all the products vary as a function of the nature of Ar and the anion X in the copper(II) salt. Thus, when $PhTl(OAc)ClO_4$ is treated with copper(II) chloride in acetic acid, the main product is chlorobenzene (yield 56–59%), but a small amount of benzene and biphenyl (2–4%) is also formed. On the other hand, mainly anisole (30–65%) and only 2% of chloroanisole are obtained from p-$MeOC_6H_4Tl(OAc)ClO_4$, while bianisyl is absent. The interaction of $PhTl(OAc)ClO_4$ with copper(II) acetate results in the formation of only benzene (13%) and biphenyl (2%).[156] The reaction with copper(I) or copper(II) cyanide leads to benzonitrile[53], while phenyl thiocyanate is formed in 42% yield in the reaction with copper(II) thiocyanate[171]. It is interesting that in the latter case the addition of potassium thiocyanate diminishes the yield of PhSCN and the yield of benzene then increases from 0 to 19%. However, the observed effect of the common ion has not been explained[173].

We may note that even copper(I) halides initiate the decomposition of organic compounds of thallium(III). Thus the interaction of CuBr with β-methoxyphenylethylthallium diacetate in acetonitrile yields the corresponding bromo-derivative[174] and it has been established with the aid of radical traps that free radicals are involved in its formation[175]. It is believed that the copper(I) halide behaves as the reductant in this reaction, converting the thallium(III) compound into an intermediate containing thallium(II).[176] The latter decomposes with formation of a radical which is oxidised further by the copper(II) halide:

$$R{-}C(OMe)HCH_2{-}Tl^{III}(OAc)_2 \xrightarrow{CuX^-} [R{-}C(OMe)HCH_2{-}Tl^{II}(OAc)_2]^- \cdot \rightarrow R{-}C(OMe)HCH_2^{\bullet} + Tl^{I}(OAc)_2^- ,$$

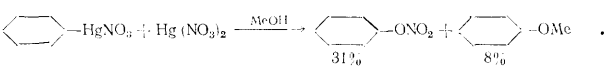
$$R{-}C(OMe)HCH_2^{\bullet} + CuX_2 \longrightarrow R{-}C(OMe)HCH_2X + CuX .$$

However, the radical reaction pathway obtains at 80 °C. Under milder conditions, the reaction has a predominantly ionic mechanism. It has been shown in relation to *erythro*-n-$C_8H_{17}CH(OMe)CHDTl(OAc)_2$ that at 60 °C the reaction takes place with inversion of configuration[176].

The data presented show that the oxidation of phenyl compounds of thallium(III) by copper(II) salts differs from the oxidation of derivatives of other metals—particularly by the fact that one-electron oxidation products can be obtained in considerable amounts in reactions with copper(II) halides. The cause of these differences is associated with the fact that the thallium in these compounds exists in the highest valence state and is a powerful electron acceptor. However, the true mechanism of these reactions is so far not clear and the substitution mechanism put forward by Ichikawa and coworkers[55,156,172] is to a large extent hypothetical.

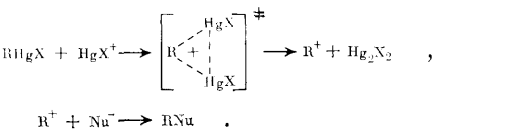
2. Oxidation of Mercury Salts

Certain electrophilic substitution reactions of organometallic compounds with bivalent mercury salts are accompanied by the formation of two-electron oxidation products. In a number of instances the process is dominant. For example, the interaction of benzylmercury nitrate with mercury(II) nitrate results in the formation of benzyl nitrate and benzyl ethyl ether in methanol and of benzyl alcohol, benzyl nitrate, and benzaldehyde in water[177,178]. The reaction with cyclohexylmercury nitrate in methanol takes place similarly, the corresponding nitrate and ether also being obtained:



According to Ichikawa and Ouchi[179], the reaction of organomercury acetates with mercury acetates likewise leads to the formation of organic acetates and a mercury(I) salt.

So far little is known about the mechanism of these reactions. It is most likely that it involves a special type of oxidative demetallation (see subsection 5 below), in which the organic group is oxidised with the simultaneous participation of the two mercury atoms. Since the rate of reaction increases following the addition of strong inorganic acids[179], presumably it involves the participation of the species HgX^+, which has a greater oxidising capacity than HgX_2:



It was noted that the interaction of propylboronic acid with mercury(II) chloride in water leads to the formation of propyl chloride and calomel together with propylmercury chloride[180]. The authors[180] believe that propyl chloride is obtained on oxidation of the transmetallation product—propylmercury chloride:

$$PrB(OH)_2 + HgCl_2 + H_2O \rightarrow PrHgCl + B(OH)_3 + HCl ,$$
$$PrHgCl + HgCl_2 \rightarrow PrCl + Hg_2Cl_2 .$$

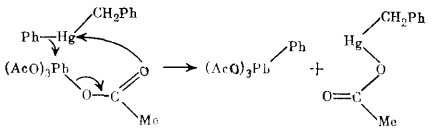
When organic derivatives of titanium(IV) ($MeTiCl_3$ [181] or Cp_2TiPh_2 [182]) react with mercury(II) chloride, calomel is formed as one of the products. According to the authors[182], the organotitanium compound decomposes and the new organic derivative of titanium(II) formed is oxidised by mercury(II) chloride:

$$Cp_2TiPh_2 + HgCl_2 \xrightarrow{CCl_4} Cp_2TiCl_2 + PhHgCl + PhCl + Ph_2 + Hg_2Cl_2 ,$$
$$Cp_2TiPh_2 \rightarrow Cp_2Ti + 2Ph^{\bullet},$$
$$n\,Ph^{\bullet} \xrightarrow{CCl_4} PhCl + Ph_2,$$
$$Cp_2Ti + HgCl_2 \rightarrow Cp_2TiCl_2 + Hg_2Cl_2 .$$

3. Oxidation by Lead-Tetra-acetate

The oxidation of organometallic compounds, particularly mercury derivatives, by lead tetra-acetate was first carried out by Criegee et al.[183] The reaction of alkyl derivatives of mercury leads to the formation of the corresponding alkyl acetates, both primary and secondary acetates being formed from primary alkylmercury acetates, which indicates the intermediate formation of carbonium ions. Thus the acetates derived from benzyldimethylmethanol and t-pentyl alcohol were isolated in the oxidation of dineophyl- and dineopentylmercury instead of the corresponding neophyl and neopentyl acetates[183]. The interaction of a fully asymmetric compound

(benzylphenylmercury) with lead tetra-acetate in benzene at room temperature results in electrophilic substitution and the elimination of the phenyl group, which is most nucleophilic[183]:

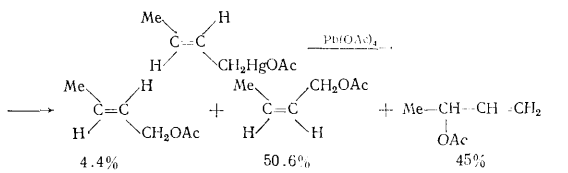


It has come to be believed that an organolead compound is always formed in the first stage of these reactions and then decomposes with formation of a two-electron oxidation product[183,184]:

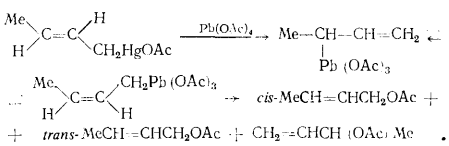
$$(PhCH_2)_2Hg \xrightarrow{Pb(OAc)_4} PhCH_2Pb(OAc)_3 \xrightarrow{-Pb(OAc)_2} PhCH_2OAc .$$

In the case of alkyl derivatives of metals, it is usually impossible to isolate the corresponding lead(IV) compound under the reaction conditions. Only the quantitative formation of $Et_2Pb(OAc)_2$ in the reaction of Et_2Hg with $Pb(OAc)_4$ in chloroform at room temperature has been described[185], but in benzene the above compound is not obtained on interaction of Et_4Sn with $Pb(OAc)_4$, ethyl acetate being produced in 78% yield[186].

All three possible isomers of the organic acetate are formed on oxidation of *trans*-crotylmercury acetate[185]:



However, the fact that much more of *cis*-crotyl acetate is formed than of the *trans*-isomer suggests that free carbonium ions do not participate in the reaction. It is most difficult to account for the preferential formation of the thermodynamically less stable *cis*-crotyl acetate. According to Kitching et al.[187], this reaction includes the following stages: transmetallation via the S_E2' (or S_Ei') mechanism, intramolecular metallotropic rearrangement of the intermediate, and oxidative demetallation of the organolead compounds formed:



The capacity of organic compounds of lead(IV) for decomposition without the oxidative demetallation mechanism depends on the nature of not only the organic group but also the anions present in solution. Thus, when potassium iodide[188] or PhMgBr [189] is added to a solution of the stable $PhPb(OAc)_3$, acid anion exchange takes place and the resulting intermediate decomposes with formation of halogenobenzenes and lead(II) salts.

It is noteworthy that the formation of products of two-electron oxidation in these reactions can occur both on oxidative demetallation of $RPb(OAc)_3$ and as a result of homolytic decomposition with cleavage of the R–Pb bond and subsequent oxidation of the radical R$^{\cdot}$ by the excess lead tetra-acetate. Presumably the oxidation of organic compounds of thallium(III) by lead tetra-acetates proceeds via one of these pathways[190]:

$$ArTl(OOCCF_3)_2 \xrightarrow[Cl_3CCOOH]{Pb(OAc)_4} ArOOCF_3 + Tl^{I} + Pb^{II} .$$

Another view on the mechanism of the formation of radicals in these reactions has been expressed in a study[191] of the oxidation of alkyl derivatives of mercury and tin by lead tetra-acetate. The reaction proceeds fairly readily on refluxing in acetic acid but the yield of the acetates is high only in the case of benzyl derivatives¶:

$$\text{n-PrHgOAc} \xrightarrow[6.5\%]{Pb(OAc)_4} \text{n-PrOAc} + \textit{cis}\text{-PrOAc} ,$$

$$\text{iso-BuHgOAc} \xrightarrow[10\%]{Pb(OAc)_4} \text{iso-BuOAc} + \text{s-BuOAc} + \text{t-BuOAc} ,$$

$$PhCH_2HgOAc \xrightarrow[82\%]{Pb(OAc)_4} PhCH_2OAc ,$$

$$(PhCH_2)_3SnCl \xrightarrow[77\%]{Pb(OAc)_4} PhCH_2OAc + PhCH_2Cl .$$

The authors[191] proposed a mechanism involving the one-electron oxidation of the organometallic compound with subsequent oxidation of the radicals and the formation of organic acetates. However, this alternative transmetallation oxidation reaction is not supported by any evidence.

On the other hand, the oxidation of trialkylboranes by lead tetra-acetate in benzene apparently proceeds via an electron transfer stage[193]. The point is that secondary radicals and not primary radicals, as is usually the case in transmetallation reactions, are preferentially split off in this reaction. For example, the amount of n-hexyl acetate formed in the reaction of bicyclohexyl-n-hexylborane with $Pb(OAc)_4$ is 10 times smaller than that of cyclohexyl acetate. This is apparently due to the preferential decomposition of the radical-cation with formation of a more stable secondary radical:

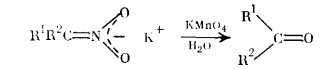
$$[C_6H_{13}(C_6H_{11})_2B]^{\cdot+} \rightarrow C_6H_{11}^{\cdot} + C_6H_{13}C_6H_{11}B^{+} .$$

4. Oxidation by Compounds of Other Metals

The oxidation of organometallic compounds by chromium trioxide apparently also proceeds via an electron transfer stage since transmetallation is hardly possible in this instance. When PhHgI and $PhCH_2HgCl$ are treated with chromium trioxide in a 1 : 1 $AcOH/Ac_2O$ mixture or in the complex $CrO_3.2Py$ in dichloromethane, iodobenzene and benzyl chloride are formed. Benzaldehyde has also been detected in the case of $PhCH_2HgCl$.[194] Tetra-alkyl derivatives of tin react with chromium trioxide in acetic acid to form aldehydes and acids[195]. The reactions of organic boronic acids with chromic acid (with CrO_3 in water) lead to the formation of an alcohol[196]:

$$\text{t-BuB(OH)}_2 + CrO_3 \xrightarrow{H_2O} \text{t-BuOH} + Cr^{III} + H_3BO_3 .$$

The oxidation of potassium salts of nitroparaffins by potassium permanganate belongs to processes of the same type[196]:



This reaction has been suggested as a method of synthesis of aldehydes and ketones.

The oxidation of tetra-alkyltin by phenanthroline complexes of iron(III) [197] and the reactions of alkyl derivatives of lead[96], tin[198], mercury[199], and platinum[200] as well as benzylcobaloxime[201] with the $IrCl_6^{2-}$ anion, which is a one-electron

¶ A high yield of alkyl acetates is observed in the reaction of $Pb(OAc)_4$ with organoaluminium compounds obtained as a result of the addition of $LiAlH_4$ to olefins in the presence of $TiCl_4$.[192] Since the reaction is not accompanied by isomerisation, it is of interest from the synthetic standpoint.

oxidant, are examples of oxidation reactions of organometallic compounds which undoubtedly proceed via a one-electron transfer stage. The products of these reactions are chloroderivatives formed as a result of the multistage two-electron oxidation with the intermediate formation of radicals. A clear confirmation of the one-electron transfer mechanism of these reactions is finding that on oxidation of, for example, a mixed lead compound $Et_{4-n}Me_nPb$, the ethyl group is split off preferentially[96] and not the methyl group as is usually the case in electrophilic substitution. Furthermore, the partial [rate?] factor for this process is independent of the number of ethyl groups in the molecule of the organolead compound, which is apparently associated with the preferential decomposition of the radical-cation via the mechanism

$$[(Et_{4-n}Me_n)Pb]^{+\cdot} \rightarrow Et^{\cdot} + (Et_{3-n}Me_n)Pb^{+} \quad .$$

The intermediate formation of radicals in the reaction of R_4Pb with $IrCl_6^{2-}$ has been demonstrated with the aid of "radical trapping agents" of the type of nitrosoisobutane[96]. Since only alkyl chlorides are formed in the reaction, one must suppose that the radicals are oxidised very rapidly.

An additional confirmation of the one-electron transfer mechanism is provided by the satisfactory linear correlation between the logarithms of the rate constants for the oxidation of organometallic compounds and their ionisation potentials[96,202,203] as well as the [absorption] frequencies corresponding to charge transfer to the complex from tetracyanoethylene[203,204]. Analysis of these correlations from the standpoint of the Marcus theory demonstrated that these reactions have an electron transfer mechanism[196,201]. It has been shown, for example, that the reaction of R_4Sn with phenanthroline complexes of iron(III) takes place as an outer-sphere transfer, while the oxidation of R_4Sn by $IrCl_6^{2-}$ involves an inner-sphere electron transfer.

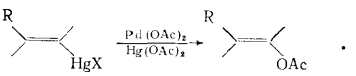
The reaction of benzylchromium $[PhCH_2Cr(H_2O)_5]^{2+}$ with iron(III), cobalt(III), and copper(II) salts, which leads to the formation of typical oxidation products of the benzyl fragment, namely benzaldehyde, benzyl alcohol, and bibenzyl, has an interesting mechanism[205]. However, kinetic study showed that the rate of this process is not determined by the electron transfer stage, since the reaction is of first order with respect to the benzylchromium cation and of zero order with respect to the oxidant. The authors[205] suggest that the rate-limiting stage of the process is the homolysis of the benzylchromium cation and that the radical fragments formed are oxidised in the rapid stage.

Using a combination of two oxidants [a palladium salt in a catalytic amount and one of the oxidants in the series comprising chromium(VI) salts, $Pb(OAc)_4$, $NaClO_3$, $KMnO_4$, $NaNO_3$, and $NaNO_2$], it was possible to achieve an interesting two-electron oxidation of phenylmercury salts. The reaction products in the presence of freshly added nucleophiles Nu^- are substituted benzenes PhNu, while in the absence of oxidants the main product of the stoichiometric reaction is biphenyl[206]:

$$PhHgOAc \xrightarrow[K_2Cr_2O_7]{Pd(OAc)_2} \underset{50\%}{PhOAc} + \underset{6\%}{Ph_2} \quad ,$$

$$PhHgOAc \xrightarrow[LiOAc]{Pd(OAc)_2} \underset{\sim 5\%}{PhOAc} + \underset{95\%}{Ph_2} \quad .$$

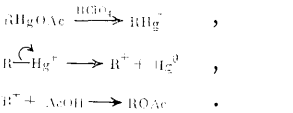
It has been suggested that transmetallation results in the formation of a phenylpalladium(II) salt which is subsequently oxidised by the main oxidant. The catalytic cycle terminates by the addition of the nucleophile Nu^- to the phenylcarbonium ion formed. The vinylmercury salts are similarly oxidised by mercury(II) acetate, the reaction being catalysed by palladium(II) acetate[207]. The reaction proved to be a convenient preparative method of synthesising substituted enol acetates:



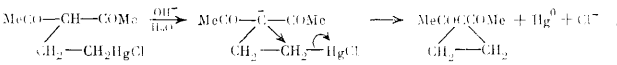
Another possible reaction mechanism is the oxidation of C_6H_5HgX or C_6H_5PdX with a palladium(IV) salt[206], obtained by the reaction of the palladium(II) salt with the main oxidant. In his analysis of this possibility, Henry[206] drew attention to the fact that, in the oxidation of an oxidant weaker than palladium(IV) such as copper perchlorate, alkyl chlorides are formed from alkyl derivatives of palladium(II), while radical coupling products are obtained from aromatic derivatives of palladium(II). Since it is difficult to suppose that PhPdX is oxidised with greater difficulty than AlkPdX, it follows from the data presented that the PhPdX oxidation reaction competes with the coupling reaction only when sufficiently strong oxidants are employed.

5. Oxidative Demetallation Reactions

The decomposition of unstable organic compounds of metals with formation of two-electron oxidation products is of special interest. The reaction involving the elimination of mercury from organomercury cations in the presence of acids is an example of such a process[179,208–210]:



A mercury elimination reaction under the influence of bases is known[211]:



This reaction is unusual, since the carbanion formed in it formally substitutes the $HgCl^-$ group by an intramolecular nucleophilic mechanism.

The acetolysis of mercury benzylmercaptide is of a type similar to that of the processes considered[212]:

$$PhCH_2SHgOAc \xrightarrow[90-100^\circ]{AcOH} PhCH_2OAc + (PhCH_2)_2 + HgS \quad .$$

The intermediate formation of the benzyl cation in this reaction has been demonstrated by trapping it with mesitylene.

The decomposition of phenylthallium bromides and iodides is in essence an oxidative demetallation reaction[213,214]:

$$PhTlBr_2 \rightarrow PhBr + TlBr \quad ,$$

$$PhTlI_2 \rightarrow PhI + TlI \quad .$$

This reaction has been suggested as a method of synthesis of aryl iodides. It has been postulated that iodobenzene is formed in the interaction of $Ph_2TlOCOCF_3$ with I_2 not only on electrophilic substitution but also as a result of oxidative demetallation[215]:

$$Ph_2Tl(OCOCF_3) + I_2 \rightarrow PhTlIOCOCF_3 + PhI \quad ,$$

$$PhTlIOCOCF_3 \rightarrow PhI + TlOCOCF_3 \quad .$$

The same pathway apparently obtains in the reactions of bismuth(V) and bismuth(III) compounds[180]:

$$Ph_3Bi(OH)_2 \rightarrow Ph_2BiOH + PhOH \quad .$$

The intramolecular decomposition of unstable organopalladium intermediates, formed in the interaction of palladium(II) salts with organometallic compounds, also constitutes an oxidative demetallation reaction, because it yields metallic palladium. For example, when $PdCl_2$ interacts with β-chloromercuriethanol or β-chloromercuriethyl acetate, acetaldehyde and vinyl acetate are formed respectively[216]:

$$HO{-}CH_2CH_2HgCl \xrightarrow{PdCl_2} \left[ClPd{-}CH_2{-}\underset{H}{CH}{-}OH\right] \rightarrow MeCHO + Pd^0 ,$$

$$MeCO{-}CH_2CH_2HgCl \xrightarrow{PdCl_2} \left[ClPd{-}CH_2{-}\underset{H}{CH}{-}\underset{O}{OCMe}\right] \rightarrow CH_2{=}CH{-}OAc + Pd^0 .$$

The nature of the products formed suggests that the decomposition of the organopalladium intermediate entails the generation of carbonium ions, which are stabilised as a result of a hydride shift (on formation of acetaldehyde) or the elimination of a proton (on formation of vinyl acetate).

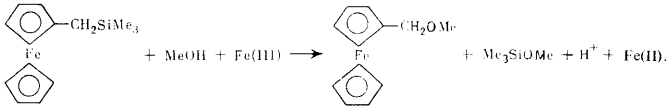
The decomposition of organometallic compounds accompanied by the intramolecular oxidation of the organic group is naturally possible only for compounds containing a metal capable of effecting two-electron oxidation. There is no doubt that this process depends both on the nature of the organic group and on the coordination environment of the metal atom. For example, the mode of the decomposition reaction of β-methoxyphenylethylthallium diacetate in aqueous methanol in the presence of perchloric acid depends on the concentration of the added chloride ions[217]. Whereas at low Cl^- concentrations oxidative demetallation, accompanied by the migration of the phenyl group, takes place and the rate of reaction increases with increasing Cl^- concentration, i.e.

$$PhCH(OMe)CH_2Tl(OAc)_2 \xrightarrow[MeOH]{Cl^-,H^+} PhCH_2{-}CH(OMe)_2 + Tl^I ,$$

at high Cl^- concentrations, where the acetate ions are fully substituted by chloride ions, the product is styrene and the rate of reaction is independent of the Cl^- concentration and is determined solely by the acidity of the medium:

$$PhCH(OMe)CH_2Tl(OAc)_2 \xrightarrow{Cl^-} PhCH(OMe)CH_2TlCl_2 \rightarrow$$
$$\xrightarrow{H^+} PhCH(\overset{+}{O}Me)CH_2TlCl_2 \rightarrow PhCH{=}CH_2 + Tl^{III} .$$

An interesting instance of oxidative demetallation has been observed by Kumada and coworkers[218,219] in studies of the solvolysis of ferrocenylmethyl derivatives of silicon and germanium in methanol, initiated by iron(II) salts:



According to the authors, methoxymethylferrocene is formed as a result of consecutive intermolecular and intramolecular electron transfers:

$$FcCH_2MMe_3 + Fe^{III} \rightarrow Fc^+{-}CH_2MMe_3 + Fe^{II} ,$$
$$Fc^+CH_2MMe_3 + CH_3OH \xrightarrow{slow} Fc{-}\dot{C}H_2 + MeOMMe_3 + H^+ ,$$
$$FcCH_2^{\cdot} + Fe^{III} \rightarrow [Fc^+{-}CH_2^{\cdot}] + Fe^{II} ,$$
$$[Fc^+{-}CH_2^{\cdot}] + MeOH \rightarrow FcCH_2OMe + H^+ .$$

The absence of a correlation between the rate constants for the solvolytic reaction and the oxidation-reduction potentials of substituted ferrocene derivatives indicates, according to the authors[218], that the rate-determining stage of the process is nucleophilic attack by methanol on the metal atom in the ferrocenium ion.

We shall consider yet another pathway leading to the formation of the two-electron oxidation products, which is possible for organic derivatives of transition metals, particularly for alkylcobaloximes. According to Anderson et al.[220], the one-electron oxidation of organocobalt compounds results in the formation of an intermediate containing a metal atom in a higher valence state. As a result of this, the electron density at the α-carbon atom is reduced so much that the carbon–cobalt bond is broken on nucleophilic substitution via the S_N2 mechanism:

$$RCo^{III}L_2 \xrightarrow{-e^-} [RCo^{IV}L_2] \xrightarrow[-Co^{II}L_2]{Nu^-} RNu .$$

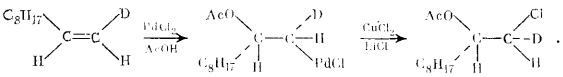
The studies of the composition of products as a function of the nature of the nucleophilic species present in solution and competing for the intermediate formed[201] as well as stereochemical data in general confirm this view. Thus it has been shown that the oxidation of (+)-*S*-(1-methylheptyl)bis(dimethylglyoximato)pyridinecobalt(III) with a two-fold excess of $IrCl_6^{2-}$ in the presence of bromide ions results in the formation of (−)-*S*-1-methylheptyl bromide in 37% yield and with an optical purity in excess of 50%,[220] i.e. the configuration at the carbon atom is inverted. However, in this formulation of the experiment one cannot rule out the possibility that the active agent in the reaction might have been the bromine formed on oxidation of Br^-. This deficiency was taken into account in a study[221] where 1-methylheptylbis(dimethylglyoximato)cobalt was oxidised at a low temperature with a cerium(IV) salt and then chloride ions were added to the reaction mixture:

$$RCo^{III}(dmgH)_2 \xrightarrow[MeOH]{CAN,\ -60^\circ} RCo^{IV}(dmgH)_2 \xrightarrow{Cl^-} RCl ,$$

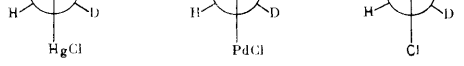
$dmgH_2 = CH_3C(=NOH)C(=NOH)CH_3$, CAN = cerium ammonium nitrate

The degree of inversion of the configuration was 90 ± 10%.

It is noteworthy that the mechanism of the oxidation of organometallic compounds examined above, which includes a nucleophilic substitution stage activated by electron transfer, has been widely used recently to account for the inversion of the stereochemical configuration in electrophilic substitution reactions involving transition metals[222]. Apparently the inversion of configuration on cleavage of the C–Pd bond with copper(II) chloride, which has been observed by Backvall[223], can be explained from the same standpoint.



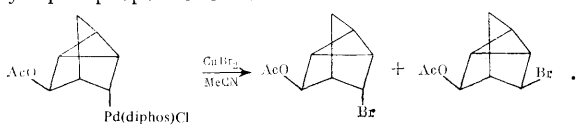
Presumably the palladium intermediate formed, whose *threo*-configuration is determined by the stereochemistry of the oxypalladisation reaction[224,225], is oxidised by $CuCl_2$ and attack by Cl^- comes from the side opposite that of the metal. It is possible to explain similarly the inversion of configuration observed in the oxidation of *threo*-3,3-dimethylbutyl-1,2-d_2-mercury chloride with copper(II) chloride in the presence of $PdCl_4^{2-}$.[226] It is believed that this reaction involves the formation of *threo*-3,3-dimethylbutyl-1,2-d_2-palladium chloride as the palladium intermediate:



Thus it is seen from the above examples that the oxidation of organopalladium compounds by copper(II) halides can bypass the transmetallation stage. Henry, who investigated

the oxidation of but-2-ene by copper(II) chloride in the presence of $PdCl_2$, reaches the same conclusion[227].

On the other hand, judging from the stereochemical results of certain reactions of organopalladium compounds with copper(II) halides, the latter proceed like those involving non-transition metal compounds, i.e. via stages involving transmetallation and the intermediate formation of radicals. An example of such reactions is provided by the interaction of *endo*-norticyclenylpalladium(II) with $CuBr_2$, which leads to the formation of the *endo*- and *exo*-isomers in approximately equal proportions[169]:



Interesting reactions occur in the oxidation by copper(II) chloride of alkyl and aryl alkyl σ-derivatives of iron [η^5-Cp.$(CO)_2$FeR]. For example, the reaction of the benzyl derivatives with $CuCl_2$ in CH_2Cl_2 results in the formation of benzyl chloride only[228]:

$$\eta^5\text{-CpFe(CO)}_2\text{CH}_2\text{Ph} + \text{CuCl}_2 \rightarrow \eta^5\text{-CpFe(CO)}_2\text{Cl} + \text{PhCH}_2\text{Cl} + 2\text{CuCl} \quad .$$

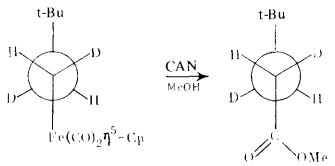
This reaction can be modelled by the electrochemical oxidation of $RFe(CO)_2\eta^5$-Cp (R = Me, $PhCH_2$, or $PhCH_2CH_2$) in the presence of chloride ions, whereupon the corresponding chloro-derivatives are also formed. It has been shown in relation to *threo*-PhCHDCHD-Fe$(CO)_2\eta^5$-Cp [228] that the electrochemical oxidation takes place with the preferential retention of configuration. Since the label is distributed between both carbon atoms of the ethyl fragment in the oxidation of the ^{13}C- labelled β-phenylethyl derivative, presumably a phenonium ion is formed in the reaction and the observed stereochemical result (retention of configuration) is due to attack by a chloride ion from the side of the iron atom.

When the same iron complexes are oxidised in alcohol and not in CH_2Cl_2, particularly in the presence of CO, carbonylation products (alkyl carboxylates) are formed[229]:

$$\text{RFe(CO)}_2\eta^5\text{-Cp} \xrightarrow[\text{R'OH,CO}]{\text{CuCl}} \text{RCOOR'} \quad ;$$

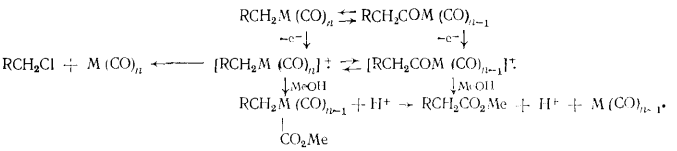
$$\text{R} = \text{PhCH}_2\text{CH}_2,\ \text{cyclo-C}_6\text{H}_{11}\text{CH}_2,\ \text{cyclo-C}_6\text{H}_{11} \quad .$$

A similar reaction takes place in the oxidation of *erythro*-3,3-dimethylbutyl-1,2-d_2-Fe(CO)η^5-Cp by cerium ammonium nitrate in methanol[230]:



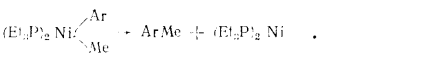
The stereochemistry of this process and also the reaction with $CuCl_2$ considered above[229] shows that the oxidation of the complex causes the insertion of CO in the C—Fe bond, which takes place with retention of configuration, after which nucleophilic attack on the alcohol takes place.

The oxidation of *p*-fluorobenzyl (R) derivatives of molybdenum, chromium, iron, manganese, namely π-$Cp(CO)_3$MoR, π-$Cp(CO)_3$CrR, π-$Cp(CO)_2$FeR, and $RMn(CO)_5$, by cerium(IV) salts in methanol in the presence of LiCl was considered from the same standpoints[231]. Apart from *p*-fluorobenzyl chloride, methyl *p*-fluorophenylacetate is formed in the reaction, the ratio of the yields of the products depending on the nature of the metal atom. The following mechanism accounts for the possible pathways leading to their formation:



Finally we shall turn to the coupling reactions which occur in the oxidation of transition metal compounds $R^1R^2ML_n$ and lead to the formation of the dimer R^1R^2. We have already encountered one example of such reactions when the oxidation of the cuprates R_2CuLi by copper(II) halides was considered[143]. The $Ar_4Cu_6X_2$ clusters are oxidised similarly[232]. Here we should like to examine these reactions in greater detail and note the role which they can play in complex processes involving transition metal complexes, particularly in the cross-coupling reaction.

Morell and Kochi were some of the first investigators who drew attention to the intramolecular coupling reactions occurring in the oxidation of organometallic compounds. They observed that the intramolecular decomposition of the complexes $[Et_3P]_2[MeArNi]$ is accelerated in the presence of ArBr or O_2.[123,233]



On the basis of these data, it was suggested that the reductive elimination can be activated by electron transfer from the complex to ArX and that ArX yields an oxidative addition product in the mechanism proposed for the decomposition:

$$L_2NiArCH_3 + ArX \rightleftarrows [L_2NiArCH_3]^{\pm} + Ar^{\cdot}X^{\cdot-} \quad ,$$

$$[L_2NiArCH_3]^{\pm} \rightarrow ArCH_3 + L_2Ni \quad ,$$

$$L_2Ni^{\pm} + ArX^{\cdot-} \rightarrow L_2NiArX \quad .$$

Generally speaking, this hypothesis was not confirmed, but data exist showing that intermediates capable of reductive elimination can be formed in the oxidation of transition metal complexes. Thus only coupling products are formed in the oxidation of dialkyl derivatives of iron(II) by a wide variety of reagents, such as Na_2IrCl_6 or thallium(III), cerium(IV), and cobalt(III) triflates[234]:

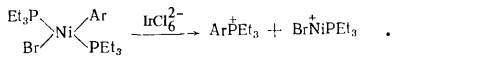
$$R_2Fe(bipy)_2 + 2IrCl_6^{2-} \rightarrow R_2 + FeCl_2(bipy)_2 + 2IrCl_6^{3-} \quad .$$

This reaction is not intermolecular and proceeds without the involvement of free radicals, because the decomposition of a mixture of the diethyl and dimethyl complexes does not result in the formation of propane. Halogens behave in a very unusual manner in the reaction considered—they exhibit exclusively oxidising properties and alkanes are formed in this instance instead of alkyl halides[130,234]:



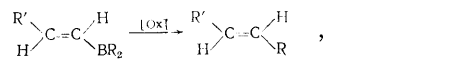
The above oxidative coupling reactions involving transition metal complexes can be modelled by electrochemical oxidation on platinum. Thus the electrolysis of triethylphosphine complexes of diarylnickel in acetonitrile leads to the formation of biaryl, whose yield reaches 94% in the case of $(PEt_3)_2Ni(o\text{-}MeC_6H_4)_2$. Some of the intermediates formed in the one-electron oxidation of the complexes have been detected with the aid of cyclic voltamperometry at −50 °C.[235]

An interesting coupling reaction occurs in the oxidation of the phosphine complexes of arylnickel bromide by Na_2IrCl_6, $Ce(CF_3COO)_4$, and $CuBr_2$:[234]



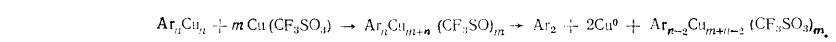
It has been shown for o-$MeC_6H_4NiBr(PEt_3)_2$ that a phosphonium cation is formed from the $[o\text{-}MeC_6H_4NiBr(PEt_3)_2]^{\ddagger}$ species, for which the corresponding EPR spectrum has been obtained at −50 °C. The same species was detected with the aid of CO and the formation of the cation $[ArCONiBr.(PEt_3)_2]^+$ was detected by EPR.

The stereospecific oxidation of alkenyldialkylboranes by $Pb(OAc)_4$, $PhI(OAc)_2$,[236] and $Pd(OAc)_2$,[237] leading to the formation of substituted olefins



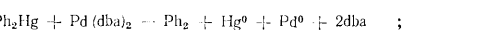
constitutes an interesting case of oxidative coupling of radicals. The Zweifel reaction, in which iodine is used as the oxidant, is a prototype of these processes[238].

The above coupling reactions, promoted by electron transfer, in essence do not differ in any way from the intramolecular thermal decomposition of organometallic compounds (reductive elimination reactions) examined in Section IV. The role of the oxidant in these reactions reduces to effecting a transition of the complex to an oxidation state which favours the occurrence of the reductive elimination reaction. However, there exist a multiplicity of reactions in which coupling takes place under the influence of compounds which function exclusively as catalysts. For example, the decomposition of the cluster compound arylcopper(I) (Ar_4Cu_4) is catalysed by copper(I) triflate. According to van Koten et al.[239], the coupling in such clusters takes place as a result of the intramolecular electron transfer in the complex formed by the reactants:

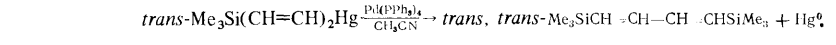


The decomposition of the clusters $R_4Cu_6X_2$ (X = Br, I, or CF_3SO_3) is promoted similarly by the addition of copper(II) salts[108,232] or copper(I) triflate[239].

Another example of such reactions is the decomposition of R_2Hg in the presence of palladium and platinum complexes in which the metal is in a low valence state[240,241]:

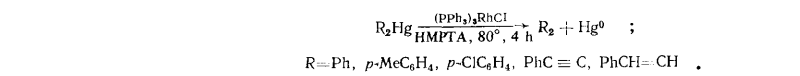


dba — dibenzylideneacetone ;

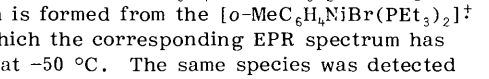


It has now been established that $Pd(PPh_3)_4$ or $Pt(PPh_3)_3$ are initially inserted in the C–Hg bond in these reactions, exhibiting the properties of a nucleophilic carbenoid. In a number of instances, when R_2Hg contains the powerful electron-accepting groups R = CF_3 and C_6H_5,[242] the insertion products can be isolated and characterised by physicochemical methods. However, the intermediates are usually unstable and undergo the elimination of mercury and reductive elimination with formation of a coupling product.

The decomposition reactions of the compounds R_2Hg catalysed by rhodium(I) complexes apparently have an analogous mechanism[243]:



We may note that similar reactions are known for organomercury salts. Thus biaryls are formed from ArHgCl on treatment with rhodium(I) complexes in the presence of LiCl.[244] The carbenoid insertion of the rhodium(I) atom in the C–Hg bond apparently takes place in this instance and Ar_2 is formed as a result of reductive elimination:



As in the instances considered above, mercury is the oxidant in this catalytic process, its oxidation state changing from +2 to 0 in the course of the reaction.

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The Mechanism of the Photolysis of Certain Hydrocarbons by Vacuum Ultraviolet Radiation

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The results of studies of the photolysis by vacuum ultraviolet radiation of saturated hydrocarbons and hydrocarbons containing individual double bonds are examined and characteristics of the photolysis of these classes of substances are discussed as a function of the molecular structure, the phase state of the given substance, and the wavelength of the radiation.
The bibliography includes 104 references.

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I. INTRODUCTION

The study of the photochemical reactions of hydrocarbons under the influence of vacuum ultraviolet radiation constitutes a branch of chemistry which has been vigorously developing in the last 15–20 years. The interest in this field is due to a number of causes.

Firstly, vacuum ultraviolet radiation constitutes an appreciable proportion of the solar radiation spectrum in the upper layers of the Earth's atmosphere and outside its limits. In particular, it is responsible for the ionisation and dissociation of atmospheric gases and for photochemical reactions involving the molecules of atmospheric contaminants. Changes in the composition of the atmospheres of other planets of the solar system also occur under the influence of vacuum ultraviolet radiation, since molecules of greatest geochemical interest absorb only this light (for example, methane, an important component of the atmosphere of Jupiter, absorbs light with $\lambda < 143$ nm [1]). Evidently, this radiation can influence significantly the physicochemical surface characteristics of the materials of flying machines in the upper layer of the atmosphere and in space; therefore the determination of the general characteristics of the effect of vacuum ultraviolet radiation on polymers is of considerable interest from the standpoint of the development of the scientific foundations of materials science.

Secondly, vacuum ultraviolet radiation is one of the significant factors acting on matter when materials, including polymers, are treated in a plasma[2].

Thirdly and finally, the study of the chemical consequences of the action of vacuum ultraviolet radiation is important for high-energy chemistry in general. Depending on the wavelength of the active light, various electronic states of molecules are excited and at shorter wavelengths (with photon energy in excess of 10–15 eV) the substance is photoionised; studies of the reactions occurring under these conditions permit inferences about the properties of the photochemical reactions of various neutral electronically excited states and ionised states of molecules. Such information is of interest for many branches of high-energy chemistry, for example, for plasma chemistry and radiation chemistry.

The aim of the present review is to examine the fundamental features of the photolysis of paraffinic and olefinic hydrocarbons in the vacuum ultraviolet region i.e. in the spectral region corresponding to intrinsic absorption by these substances. Particular attention has been concentrated on the comparative study of the photolysis of gaseous, liquid, and solid hydrocarbons.

II. CHARACTERISTIC FEATURES OF THE EXPERIMENT

Active research in the vacuum ultraviolet region has been prosecuted only during the last two decades because only comparatively recently the necessary optical materials, transparent in the wavelength range 105–160 nm, sufficiently powerful light sources in this region, and the corresponding spectroscopic apparatus have become available for experiments[3].

Optical Materials

The optical components of apparatus designed for research in the vacuum ultraviolet region must be made of substances transparent to this type of radiation. Such substances are LiF, CaF_2, MgF_2, BaF_2, SrF_2, LiO, BeO, and sapphire[3,4]. However, these substances are opaque to light with $\lambda < 105$ nm so that studies in the above spectral region are still more difficult. However, the use of various substances in the form of thin film permits experiments also at $\lambda < 105$ nm. The choice of substances suitable for the preparation of thin transparent films which can be used to make windows in photochemical cuvettes or filters depends on their absorption coefficients in the experimental region and also on their mechanical properties. The films are obtained from organic substances or metals[4].

Light Sources

The main requirement which must be met by photochemical light sources is high radiation intensity (not less than 10^{13} to 10^{14} quanta s^{-1}), which is dictated by the sensitivity of modern analytical methods and the limited amount of time available. It is desirable to have a monochromatic light source, which permits the generation in the test specimen of quite definite excited electronic or ionic states. Various monochromatic radiation sources in the vacuum ultraviolet region, operating on the basis of various types of electric

discharge (ultrahigh frequency, high frequency, arc, spark, and glow discharges) in the inert gases (Xe, Kr, Ar, Ne, and He) and in molecular gases (Br_2, I_2, N_2, etc.) have now been developed and used.

Electrodeless resonance lamps, in which the discharge is maintained with the aid of a decimetre wave generator, have been most widely used in the last decade[1,5,6]. Xenon and krypton arc discharge resonance lamps (of types of KSR-1, KSR-2A, KRR-2A) are manufactured in the USSR.[7,8] In addition, synchrotron radiation, i.e. the electromagnetic radiation of electrons moving in a circular orbit with a velocity close to that of light, can be employed as the source of vacuum ultraviolet radiation[4,9]. The continuous spectrum of synchrotron radiation extends from the near infrared to hard X-rays. The intensity of the radiation is stable and is calculated in absolute units, which permits its employment as a standard light source. The radiation is polarised (degree of polarisation approximately 85%; the electric vector lies in the plane of the electron orbit). In order to isolate monochromatic light, monochromators are used; the intensity of the vacuum ultraviolet radiation, for example, that of the DEZI synchrotron (Hamburg, Federal Republic of Germany) at the outlet slit of the monochromator then reaches ~10^{12} quanta s^{-1} nm^{-1}.[9]

Detectors of Vacuum Ultraviolet Radiation

A whole series of detectors are used to detect vacuum ultraviolet radiation: photoelectric detectors, thermophosphors, photographic plates, and ionisation chambers[4]. Photochemical actinometry is also widely used. One of the easiest and commonest methods of measuring the absolute radiation intensities is photochemical gas actinometry, i.e. the determination of the intensity of the light generated by the source from the known yield of gaseous products of photochemical reactions. The following actinometric systems may be noted: the decomposition of carbon dioxide[4,10] or hexafluoroacetone[11] with formation of CO; the formation of O_3 in the photolysis of O_2,[12] the formation of H_2 and C_2H_2 in the photolysis of C_2H_4,[13] the formation of NO in the photolysis of N_2O,[14] the formation of H_2 on irradiation of HBr,[15] etc.[1,4,15].

Analytical Methods for the Products of Photochemical Reactions

The analysis of the products of the photolysis of hydrocarbons by vacuum ultraviolet radiation requires the application of extremely sensitive analytical methods, particularly in the photolysis of solids. On the one hand, this can be accounted for by the low intensity of the radiation from the existing light sources (~10^{14}–10^{15} quanta s^{-1}). On the other hand, the changes in polymeric materials lead to the accumulation of products in a very thin layer (~100 to 200 nm [16,17]) even after long photolysis times, and even high concentrations of these products can be detected only with the aid of sensitive methods. Gas and liquid chromatography, mass spectrometry, optical absorption spectroscopy in the vacuum ultraviolet region, multiple diffuse total internal reflection infrared spectroscopy, and EPR are used nowadays for the qualitative and quantitative detection of the products of the vacuum ultraviolet photolysis of hydrocarbons[5,16–21].

III. PHOTOLYSIS OF SATURATED HYDROCARBONS

1. Optical Spectroscopy

The threshold in the absorption of light by saturated hydrocarbons is near 7–8 eV. With increase of the number of carbon atoms in linear alkanes, the light absorption threshold shifts from ~143 nm for methane[1,22] towards longer wavelengths (Fig.1). The absorption threshold for polyethylene (Fig.2) is observed at 160–165 nm [23,24] (at longer wavelengths the optical density is mainly due to light scattering[23]). It is believed[22] that the first absorption band of alkanes is due to the $\sigma \rightarrow \sigma^*$ excitation of the electrons of the C–C bond, while the C–H bond begins to absorb light with $\lambda \lesssim 143$ nm. However, it has been suggested[26,27] that the first absorption band is due to Rydberg transitions to 3*s* and 3*p* orbitals. The transition takes place from two close molecular orbitals: $1e_g$ and $3a_g$ (Sandorfy[27]); the $1e_g$ molecular orbital is strongly bonding for the C–H bond and is antibonding for the C–C bond, while the $3a_{1g}$ orbital is weakly C–H bonding and is strongly C–C bonding. Mulliken[26] believes that the difference between the Rydberg transitions and the transitions of the valence shell electrons is in this case merely semantic and in reality these two types of transitions are coupled.

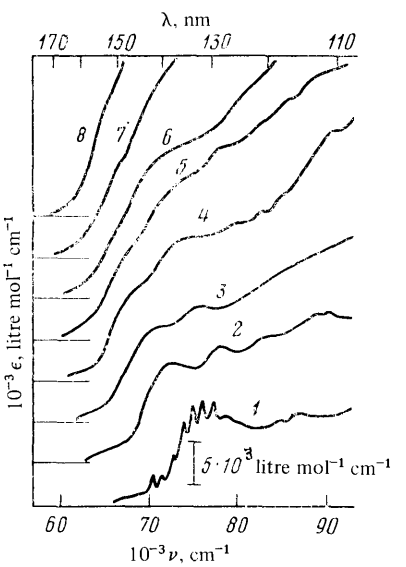


Figure 1. Absorption spectra of linear alkanes in the gas phase[22]: *1)* C_2H_6; *2)* C_3H_8; *3)* C_4H_{10}; *4)* C_5H_{12}; *5)* C_6H_{14}; *6)* C_7H_{16}; *7)* C_8H_{18}; *8)* C_9H_{20}.

The study[25] (Fig.2) of the absorption spectra of polyethylene (PE) and the normal paraffins $C_{28}H_{58}$ and $C_{42}H_{86}$ at 4.2 K led to the discovery of a peak with $\lambda_{max} \cong 148$ nm, which is not observed at room temperature. The authors[25] assigned it to a transition due to a Vanier exciton. Partridge[23,28–31] believes that the entire PE absorption band is due to the exciton interaction. On irradiation with $\lambda \cong 125$–100 nm light, the C_1–C_8 alkanes begin to ionise in

the gas phase. For photon energies near the ionisation threshold, the ionisation quantum yield is low, but, with increase of the photon energy, it rises and, for low-molecular-weight alkanes and light with $\lambda \cong 83-78$ nm, it is unity[32]. In the absorption spectra this region has the form of a broad maximum at the above wavelengths (~80 nm). The absorption intensity then falls monotonically to ~28 nm.[26]

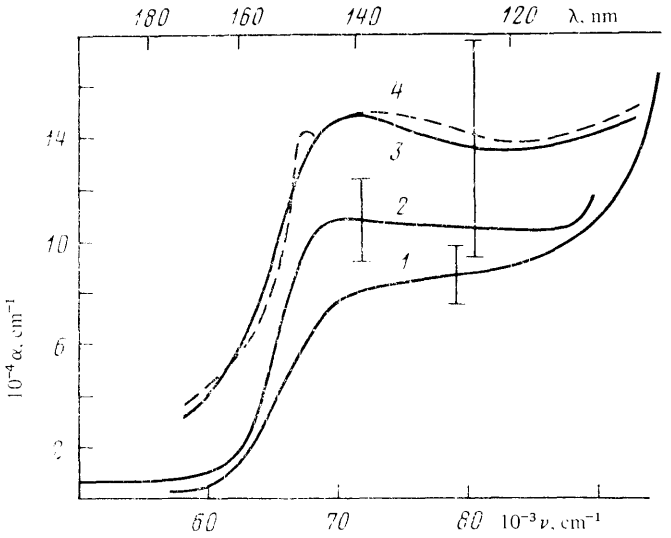


Figure 2. Absorption spectra of polyethylene: *1*)–*3*) at room temperature (data from Refs. 23–25 respectively); *4*) at 4.2 K;[25] α = decadic absorption coefficient.

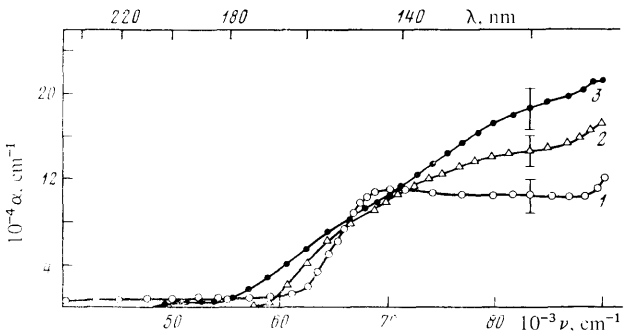


Figure 3. Absorption spectra: *1*) polyethylene; *2*) polypropylene; *3*) polyisobutylene[24]; α = decadic absorption coefficient.

The spectra of highly branched saturated hydrocarbons exhibit a bathochromic shift of the edge of the absorption band relative to the spectra of linear hydrocarbons owing to the decreased energy of the first excited state[33].

In the theory of the absorption spectra of branched alkanes in the gas phase it is assumed that the excited states are degenerate[22], but in reality this degeneracy is removed. For example, for isobutane two transitions are observed instead of one transition (as for propane), the two transitions being symmetrically displaced relative to the transition frequency in propane; for neopentane, three transitions are observed instead of one[22].

Analogous changes have been observed also on comparing the absorption spectra of polymers: PE, polypropylene (PP), and polyisobutylene (PIB) [24] (Fig. 3). To account for this, Raymonda and Simpson[22] and Dorofeev and Skurat[24] resorted to the Jahn–Teller theorem, according to which the degeneracy of the excited state is removed when the molecular symmetry is disturbed. As a result, one observes states with higher and lower energies than those observed for linear saturated hydrocarbons.

Cycloalkanes and highly branched alkanes absorb at longer wavelengths than the corresponding linear alkanes. Thus it has been established[22] that the C_3–C_8 cycloalkanes begin to absorb light at a wavelength of ~175 nm.

The fluorescence of saturated hydrocarbons on excitation with light corresponding to the intrinsic absorption band has been investigated in a number of studies[29–32]. The observed luminescence is monomeric and not excimeric, as suggested by Antonova et al.[21], because the luminescence spectra of hydrocarbons in the vapour phase and the pure liquid hardly differ[34,36]. Furthermore, the emission does not change even in dilute solutions of hydrocarbons in various solvents frozen at 77 K.[36]

The fluorescence of hydrocarbons is characterised by the following features. The spectral distribution of the fluorescence exhibits a Gaussian dependence of the intensity on the wavenumber[37]. On excitation of the fluorescence with light at different wavelengths, its spectrum remains unaltered but the quantum yield decreases with decrease of the wavelength of the exciting light. The fluorescence spectra of saturated hydrocarbons are displaced relative to their absorption spectra by approximately 0.7–1.8 eV;[37] such a large Stokes shift indicates appreciable nuclear perturbations in the excited emitting state[36,37]; under these conditions, the position of the maximum remains unaltered as the number of carbon atoms (N_C) increases, but the fluorescence quantum yield increases (Table 1). The increase of the fluorescence quantum yield is believed[35–37] to be due to a significant decrease in the rates of certain non-radiative processes.

Table 1. The lifetimes of the excited states and the fluorescence quantum yields (liquid phase, 147 nm).[34–37]

Compound	$10^9 t$, s	$10^4 \cdot \Phi_f$	Compound	$10^4 \cdot \Phi_f$
n-Pentane	0.3	0.6	2-Methylpentane	0.001
n-Heptane	6	7	3-Methylhexane	0.007
n-Nonane	15	15	4-Methylnonane	0.028
n-Undecane		28	2-Methylundecane	0.036
n-Hexadecane	50	44		

This influence of N_C can be explained by the fact that its increase entails an increase of the lifetime of the excited states as a consequence of the delocalisation of the electronic excitation over a long chain. The potential surfaces of the ground and excited states approach one another with increase of N_C, diminishing the excitation amplitude, which reduces the probability of non-radiative transitions (including chemical processes). This explanation is consistent with the

fact that the first absorption transition of n-alkanes undergoes a bathochromic shift with increase of N_C, while the energy of the fluorescence transition remains unaltered[35-37]. After the introduction of branches into n-alkanes, the emission spectrum undergoes a bathochromic shift. Thus all the n-alkanes investigated emit light at ~207 nm, 2-methylbutane emits at 233 nm, 2-methylhexane emits at 223 nm, 2-methyloctane emits at 217 nm, etc.[37]. As mentioned above, the wavelength of the first absorption transition also increases under these conditions, but the wavelengths of the emitted light increases to a greater extent, implying that branching increases the changes in the internuclear distances in the excited state, which leads to an increase of the rate of nonradiative transitions and to a corresponding decrease of the fluorescence quantum yield (Table 1).[35,36] The fluorescence of unsubstituted cycloalkanes is observed only for cyclohexane[35,37] (at 201 nm with quantum yields of 8.8×10^{-3} and 3.5×10^{-3} on excitation with light at 165 and 147 nm respectively).

Table 2. The quantum yields of the products of primary processes in the photolysis of fully deuterated n-butane (n-C_4D_{10}).[38]

Product	147 nm	123.6 nm
$CD_4 + C_3D_6$	0.009	0.04
$\dot{C}D_2 + C_3D_8$	0.005	0.018
$C_2D_4 + C_2D_6$	0.21	0.28
$\dot{C}_2D_5 + \dot{C}_2D_5$	0.15±0.01	0.17±0.02
$\dot{C}_2D_7 + \dot{C}D_3$	0.04	0.07
$\dot{C}_4D_9 + \dot{D}$	0.05	0.06
$C_4D_8 + D_2$	0.55±0.05	0.40±0.05

2. Photolysis of Low-Molecular-Weight Hydrocarbons

The gas phase. The photolysis of alkanes in the gas phase has been studied in greatest detail for photon energies below the ionisation threshold: the yields of the products of photochemical reactions have been determined and the mechanisms of the formation of a number of substances have been deduced. Table 2 lists the products of the primary photolytic reactions of n-butane under the influence of light at 147 and 123.6 nm in the gas phase with an indication of their quantum yield. The processes and yields presented in Table 2 are typical for the photolysis of linear alkanes in the gas phase[1,32,38]. The main process in the photolysis of linear alkanes by light below the ionisation threshold involves the removal of a hydrogen molecule on decomposition of an electronically excited molecule. In addition to the elimination of a hydrogen molecule, for ethane the elimination of two hydrogen atoms has been noted:

$$CH_3CH_3 + h\nu \begin{cases} \longrightarrow H_2 + CH_3\ddot{C}H^{\neq} \\ \longrightarrow 2\dot{H} + CH_2{=}CH_2^{\neq} \end{cases}.$$

Acetylene is formed in the decomposition of excited $C_2H_4^{\neq}$:

$$C_2H_4^{\neq} \rightsquigarrow H_2 + CH \equiv CH \quad .$$

Decomposition side reactions have been noted[1] also for propane and butane.

The study of the isotopic composition of hydrogen in the photolysis of mixtures of the normal and deuterated alkanes and also of partly deuterated alkanes has shown (Table 3) that H_2 can be eliminated from both two neighbouring carbon atoms and from the same carbon atom, for example[1]:

$$CH_3CD_2CH_3 + h\nu \begin{cases} \longrightarrow H_2 + CH_3CD_2\ddot{C}H^{\neq} \\ \longrightarrow D_2 + CH_3\ddot{C}CH_3^{\neq} \\ \longrightarrow HD + CH_3\dot{C}D\dot{C}H_2^{\neq} \end{cases}.$$

In the photolysis with light at 147 nm a hydrogen atom is eliminated with a probability smaller by a factor of ~10; in the photolysis by light at shorter wavelengths the process probability increases. Overall, a decrease of the wavelength of the photolysing light entails a decrease of the overall yield of hydrogen: for example, the quantum yield of hydrogen from ethane[46] changes from 0.85 (147 nm) to 0.4 (123.6 nm). The decrease is compensated by an increase of the yields of other primary processes, for example, the dissociation of the C–C bond.

Table 3. The isotope composition (mole %) of the hydrogen formed on irradiation of partly deuterated hydrocarbons and 1 : 1 mixtures of the usual and fully deuterated hydrocarbons.

Hydrocarbon	λ, nm	H_2	HD	D_2	Refs.
CH_4+CD_4	123.6	47.3	10.5	42.2	[39]
CH_4+CD_4	*	47.4	26.4	26.2	[39]
$C_3H_6+C_3D_6$	147	58.16	3.3	38.5	[1]
$C_3H_6+C_3D_6$	*	48	24.6	27.4	[40]
CH_3CD_3	147	58.5	16.9	24.6	[1]
$C_3H_8+C_3D_8$	147	56.7	5.4	37.9	[1]
$C_3H_8+C_3D_8$	123.6	45.7	19.4	34.9	[1]
$C_3H_8+C_3D_8$	*	67.6	22.1	10.3	[41]
$CH_3CD_2CH_3$	147	24.6	22.6	52.8	[1]
$CH_3CD_2CH_3$	123.6	51.3	28.7	20.0	[1]
$C_4H_{10}+C_4D_{10}$	147	62.3	6.3	31.6	[1]
$C_4H_{10}+C_4D_{10}$	123.6	49.8	16.4	33.8	[1]
iso-C_4H_{10}+ iso-C_4D_{10}	147	56	27.3	16.7	[1]
iso-C_4H_{10}+ iso-C_4D_{10}	123.6	50.2	39.9	9.9	[1]
$(CH_3)_3CD$	147	41.6	55.5	2.9	[1]
$(CH_3)_3CD$	123.6	64.7	32.1	3.2	[1]
$(CH_3)_2CHCH_2CH_3+(CD_3)_2CDCD_2CD_3$	147	63.0	2.0	35.0	[42]
$(CH_3)_2CHCH_2CH_3+(CD_3)_2CDCD_2CD_3$	123.6	67.6	5.5	26.5	[42]
$(CH_3)_2CHCH_2CH_3+(CD_3)_2CDCD_2CD_3$	104.8—106.7	71.8	17.4	10.7	[42]
$(CH_3)_2CHCH_2CH_3+(CD_3)_2CDCD_2CD_3$	**	57.2	28.8	14.0	[42]
PE + DPE	156	79	5.2	15.8	[43]
PE + DPE	147	68.4	6.7	24.9	[43]
PE + DPE	123.6	62.8	8.9	28.3	[43]
PE + DPE	*	57.5	23.9	18.6	[44]
C_2H_4-C_2D_4 copolymer	147	67	16	17	[45]
C_2H_4-C_2D_4 copolymer	123.6	67	18	15	[45]
Cyclo-C_3H_6+ cyclo-C_3D_6	147	52.3	20.5	26.3	[1]

*Irradiation with fast electrons. **Irradiation with ^{60}Co γ-rays.

The dissociation of the C–C bond can occur with formation of both molecular and radical hydrocarbon products, for example[1]:

$$CH_3CH_2CH_3 + h\nu \begin{cases} \longrightarrow CH_4 + C_2H_4 \\ \longrightarrow \dot{C}H_3 + \dot{C}H_2CH_3 \end{cases}.$$

However, the probability of the dissociation of the C–C bond with formation of molecular hydrocarbons is greater than for the process involving the formation of radical products[1,32,38]. It is noteworthy that the dissociation of the C–C bond with formation of molecular products involves the transfer of a hydrogen atom. Experiments with partly deuterated hydrocarbons permit a determination of the relative probability of the transfer of primary, secondary, and tertiary hydrogen atoms (Table 4).

With increase of the branching of the alkanes, the yields of processes involving the dissociation of the C–C bond increase, while the yield of hydrogen falls (Tables 5–7); the fraction of HD in the hydrogen produced increases (Table 3). For cyclopropane and cyclobutane, hydrogen is formed with a low quantum yield (Table 5), as for branched alkanes, while the fraction of atomic hydrogen eliminated increases (Table 3); on the other hand, the main process is one involving the dissociation of the C–C bond:[1,38]

$$\text{cyclo-}C_3H_6 + h\nu \rightarrow C_2H_4 + \ddot{C}H_2 \ .$$

However, in the case of cyclopentane and cyclohexane the main processes involve (as for linear alkanes) the elimination of molecular hydrogen (Table 5).[38]

Table 4. The form in which alkanes are formed in the photolysis of branched alkanes $CH_3CX_2CYCZ_3$ by 147 nm light[38].

Product	Relative probabilities of formation	
	R=CH_3	R-CH_2CH_3
RY	1.0	1.0
RX	1.3	1.0
RZ	0.15	0.17

Note. X, Y, and Z denote hydrogen and/or deuterium atoms in various partly deuterated compounds. No correction was applied for the isotope effect.

Table 5. The quantum yields of hydrogen in the gas-phase photolysis of alkanes by 147 nm light[38].

Compound	Φ	Compound	Φ
CH_3CH_3	0.85	$(CH_3)_4C$	<0.05
$CH_3CH_2CH_3$	0.70	cyclo-C_3H_6	<0.02
$CH_3CH_2CH_2CH_3$	0.59	cyclo-C_4H_8	<0.02
$CH_3CH_2CH_2CH_2CH_3$	0.65	cyclo-C_5H_{10}	0.7±0.1
$(CH_3)_2CHCH_3$	~0.22	cyclo-C_6H_{12}	0.7±0.1
$(CH_3)_2CHCH_2CH_3$	~0.24		

Overall the molecular decomposition reactions of electronically excited alkanes (linear, branched, and cyclic) predominate. The decomposition quantum yields are then close to unity.

The liquid phase. A number of studies have been made on the photolysis of linear and branched alkanes in the liquid phase[5,20,21,47–49]. It has been established that the primary processes are similar to those observed in the gas phase (Tables 6 and 7). However, the secondary fragmentation of the excited molecules formed in the primary process is less important than in the gas phase. For example, in the photolysis of ethane at the temperature of liquid nitrogen, excited ethylene molecules are formed. The decomposition of these excited molecules with formation of acetylene, which plays an important role in the gas-phase photolysis, is in this case inhibited by deactivating collisions in solution[50]. As in the gas phase, the formation of hydrogen is unimportant for branched alkanes in the liquid phase (Table 7); the yields of processes involving the dissociation of the C–C bond and the formation of molecular hydrocarbon products are higher in the liquid phase than in the gas phase but the relative probabilities of these processes are approximately the same in the two cases (Table 7).

Table 6. The quantum yields of the primary products in the photolysis of n-pentane (n-C_5H_{12}) on irradiation with 147 nm light in the gas and liquid phases[20,38].

Product	Gas	Liquid
CH_4	0.01	0.01
C_2H_6	0.048	0.05
C_3H_8	0.053	0.06
H_2	0.65±0.1	0.70

Table 7. The quantum yields of the primary molecular hydrocarbon products in the photolysis of 2,2,4-trimethylpentane (iso-C_8H_{18}) in the gas and liquid phases[20,32,38].

Product	Gas		Liquid
	147 nm	123.6 nm	147 nm
CH_4	0.063	0.066	0.17
iso-C_4H_{10}	0.190	0.225	0.36
neo-C_5H_{12}	0.029	0.34	0.05
H_2	~0.1		

Overall, the different primary decomposition reactions of excited alkane molecules persist and their quantum efficiency remains high also in the liquid phase. For example, in the photolysis of liquid cyclohexane, on irradiation with light at 147 nm, the quantum yield of hydrogen is close to unity, as in the gas phase[51,52]. In the study of the photolysis of isooctane by light at 147 and 160–180 nm in the condensed phase over the temperature range 173–373 K, it was established[49] that the ratio of the yields of the photolysis products hardly changes with increase of temperature but the overall quantum yield becomes greater than unity.

3. The Photolysis of Polyolefins

Polyethylene. The photolysis of PE by light at the wavelengths corresponding to the intrinsic absorption band has been investigated in a series of studies[16,17,43,45,53–57]. It was established that the main gaseous product (and virtually the only product) of the photolysis of PE on irradiation with light at 147 nm is hydrogen[43,57]. Its initial quantum yield is 0.4 ± 0.1.[43] Hydrogen can be eliminated in the form of a molecule accompanied by the formation of a *trans*-vinylene double bond[16] (hydrogen can then be eliminated from one carbon atom or two neighbouring atoms[45]):

$$M + h\nu \xrightarrow{\Phi\simeq 0.31} H_2 + \sim CH{=}CH \sim \ ,$$

and also on elimination of the $\dot{H}$ atom[17,43,56]:

$$M + h\nu \xrightarrow{\Phi\simeq 0.06} \dot{H} + \sim \dot{C}H{-}CH_2 \sim \ .$$

The relative probability of the elimination of atomic hydrogen

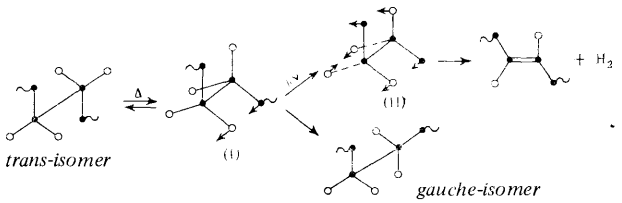
is approximately the same for solid PE as for low-molecular-weight alkanes in the gas phase. This is also indicated by a comparison of the isotopic compositions of the hydrogen formed in the photolysis of mixtures of the usual and deuterated hydrocarbons (Table 3). However, in contrast to the photolysis of simple alkanes in the gaseous and liquid phases, where $\Phi(H_2) \cong 1$, in the photolysis of solid PE pathways leading to the deactivation of the excited state of molecules without the formation of hydrogen predominate[43]. According to the authors[43], the factors responsible for the decrease of the quantum yield of hydrogen must be both transition to the solid phase, facilitating the deactivation of the electronically excited states, and the large size of the polymeric molecules, promoting the delocalisation of the excitation.

Table 8. Temperature dependence of the quantum yields of hydrogen in the photolysis of deuteropolyethylene[43,54].

t, °C	23	100	120	150	175	200	220	250
$\Phi(D_2+HD)$	0.2—0.25	0.4	0.5	0.65	0.75	0.8	0.9	0.9

The influence of temperature above room temperature on the quantum yield of hydrogen (Table 8) has also been observed[43,54], the greatest increase of the yield being noted at high temperatures even in a polymer melt. It is believed[54] that this temperature dependence indicates the elimination of molecular hydrogen from the vibrationally excited states. Presumably, the fraction of polymeric molecules having a conformation favourable for the elimination of molecular hydrogen increases with increase of temperature.

The relation between the effect of temperature in the photolysis of PE and the conformational kinetics has been explained[58] on the assumption that the transient configurations in the rotational-isomeric transition (I) and in the elimination of molecular hydrogen (II) in the $\sim CH_2-CH_2\sim$ unit in the electronically excited state are similar. In this case, the hydrogen atoms approach one another most closely and the steric conditions are most favourable for the elimination of an H_2 molecule:



According to selection rules, the probability of the absorption of a photon is a maximum for excitation of symmetrical vibrations of the unit (in the scheme above the directions of the vibrations are indicated by arrows). The planar disposition of the H–C–C–H bonds occurring in the *trans–gauche* transitions is therefore most favourable for the elimination of H_2, the transhybridisation $sp^3 \rightarrow sp^2 + p$ of carbon atoms, and the formation of a double bond. As a consequence of this stereospecificity of the process, the kinetics of slow conformational transitions partly determine (since the hydrogen molecule is also eliminated with a high probability from the same carbon atom and not only from two neighbouring carbon atoms[45]) the unusual temperature dependence of the quantum yield of hydrogen in the rapid photolysis of PE.

In the photolysis of PE by light at 147 nm, a C–C bond is also ruptured with formation of a vinyl double bond[16,17]:

$$M + h\nu \xrightarrow{\Phi \cong 0.0} \sim CH_2-CH_3 + CH_2=CH-CH_2\sim \quad .$$

It has been observed[43,45] that the hydrogen formed in the photolysis of mixtures of PE and deuterated polyethylene (DPE) is characterised by a higher [H]/[D] ratio than the mixture of polymers. This effect is due to the intermolecular transfer of excitation energy from the deuterated PE molecules to the normal molecules. Judging from the isotopic composition of the hydrogen formed, in the 1 : 1 copolymer of C_2H_4 and C_2D_4 the energy transfer from the C_2D_4 units to C_2H_4 units via the polymer chain takes place with a greater efficiency than the intermolecular transfer in the mixture of PE and DPE.

The radius of energy transfer from methylene units to *trans*-vinylene double bonds, amounting to 0.3–0.7 nm, has been calculated[57]. In the course of photolysis the quantum yields of the main products diminish: the double bonds attain a limiting concentration (4×10^{-3} mol g^{-1}), while hydrogen continuously evolves with a low (~0.02), slowly decreasing quantum yield. The observed sharp diminution of the quantum yield of hydrogen at the beginning of the photolysis is due to the transfer of excitation energy to double bonds.

The photolysis of PE is also accompanied by a cross-linking process[56,57] as a result of the recombination of the radicals formed in the course of the elimination of a hydrogen atom H and

$$\dot{H} + \sim CH_2-\dot{C}H_2 \sim \rightarrow H_2 + \sim \dot{C}H-CH_2\sim \quad .$$

As double bonds accumulate, they are also hydrogenated by atomic hydrogen:

$$\dot{H} + \sim CH=CH\sim \rightarrow \sim \dot{C}H-CH_2\sim \quad .$$

Furthermore, double bonds are consumed in the intramolecular cross-linking reaction, which leads to the attainment of their limiting concentration[17,56,59].

Polypropylene (PP). It has been established[17,60] that the photolysis of PP by light at 147 nm results in the formation of individual bonds and hydrogen in the main primary processes. The double bonds are produced on elimination of a hydrogen molecule and on degradation of the main polymer chain into molecular products:

$$M + h\nu \xrightarrow{\Phi \lesssim 0.25} H_2 + \sim \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH\sim \quad ,$$

$$M + h\nu \xrightarrow{\Phi \cong 0.25} \begin{cases} \sim CH_2CH_2CH_3 + CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}\sim \\ \sim CH_2CH=CH_2 + CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}\sim \end{cases} \quad .$$

Processes involving the elimination of a hydrogen atom,

$$M + h\nu \rightarrow \dot{H} + R$$

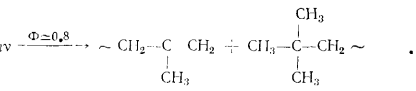
and the formation of methane,

$$M + h\nu \xrightarrow{\Phi \cong 0.025} CH_4 \quad ,$$

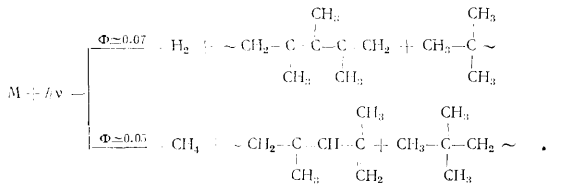
also occur. 2-Methylpropane and propene are formed in still lower yields.

In the course of its photolysis, PP undergoes cross-linking, apparently by the recombination of radicals in reactions similar to those in the photolysis of PE. However, in contrast to PE, in PP the cross-linking process is accompanied by a highly efficient degradation process, which is indicated by the decrease of the thickness of PP films during photolysis.

Polyisobutylene (PIB). In the photolysis of PIB by light at 147 nm, mainly individual double bonds and conjugated diene double bonds are formed in the primary stage[17,24]. Individual double bonds are produced on degradation of the main polymer chain:



The conjugated diene double bonds are formed in the primary process with elimination of H_2 or CH_4 and the degradation of the main polymer chain:



In the secondary stages of photolysis, gaseous hydrocarbon products are formed (2,4,4-trimethylenepentane, 2,4,4-trimethylpent-1-ene, and isobutene) with increasing quantum yields, which leads to the conversion of the surface layer of the polymer into a viscous liquid and to a decrease of the thickness of the specimen.

4. Excited States of Saturated Hydrocarbons and Their Decomposition Products

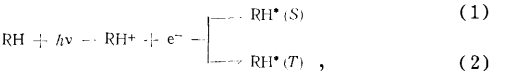
According to optical selection rules[61], in the photolysis of hydrocarbons virtually only singlet states are excited (the probability of the excitation by light of the triplet states of organic molecules without heavy atoms is $\sim 10^{-5}$).[61] However, on the basis of theoretical calculations, it has been claimed[62,63] that the rate of the intersystem crossing for alkanes, particularly in a condensed phase, is high ($\sim 10^{10}$ to 10^{11} s^{-1}). It follows from studies on the fluorescence of alkanes[34-37], examined above, that the radiative deactivation of the excited singlet state is accompanied by non-radiative deactivation processes (including chemical processes), the overall rate constant for which decreases almost linearly with increasing chain length. This suggests that the intersystem crossing cannot be very significant in long-chain alkanes.

Liquid iso-octane has been photolysed[48] by 147 nm light in the presence of 1,3-cyclohexadiene (it is known[64] that 1,3-cyclohexadiene, which is an acceptor of the donor triplet state, undergoes photochemical dimerisation in the triplet state). The 1,3-cyclohexadiene dimer was then detected and identified, but its quantum yield did not exceed 0.005, indicating that the probability of the intersystem crossing in hydrocarbons (linear and branched) is low.

The effects involving a decrease of the quantum yields of the iso-octane photolysis products as a result of combination with radicals and transfer of excitation energy to the molecules of additives (CCl_4, $C_6H_{13}Cl$, C_6F_{16}, O_2, cyclo-C_6H_8) suggest[21,48] the presence of two excited states of iso-octane, leading to the same products via mechanisms involving the molecular and radical decomposition of iso-octane molecules.

The presence of at least two electronically excited states of n-hexane, from which hydrogen is formed, is also indicated by a decrease of the quantum yield of hydrogen to a constant value of 0.65 following the addition of SF_6, compared with that observed in the photolysis of pure n-hexane[47]. It has been established that in the photolysis of hydrocarbons hydrogen is split off in the form of a molecule or atom.

Theoretical studies[62,63] have led to the conclusion that excited singlet states of alkanes are capable of decomposing with elimination of molecular hydrogen directly in the primary step, while triplet states give rise to atomic hydrogen and a free radical via a predissociation mechanism. To test this hypothesis (the elimination of atomic hydrogen from the triplet state), a study was made[55] of the isotope composition of the hydrogen formed in the photolysis of the 1:1 copolymer of C_2H_4 and C_2D_4 at 77 K by 147 and 123.6 nm light. It was established that, in the photolysis at 77 K, ~30 and 37% of the hydrogen formed is evolved directly in the course of elimination (for 147 and 123.6 nm light respectively). The residual hydrogen is evolved only in the course of heating the specimen to room temperature. It has been observed (Table 9) that the fraction of HD in the hydrogen evolved on warming the copolymer irradiated at 77 K is greater than in the hydrogen evolved directly during photolysis. Since the photoionisation of PE takes place preferentially with formation of charged pairs, like that of any other solid organic compound with a low dielectric constant, i.e.



(1)

(2)

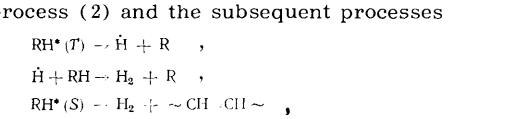
the above processes proceed via a mechanism involving the recombination of charged pairs. In this case, the ratio of the yields of reactions (1) and (2) depends on the average lifetime τ of the ion pairs relative to the recombination process[65]. For low values of τ (less than the spin relaxation time of the electron, which is $\sim 10^{-6}$ s), the charged pair recombines only via mechanism (1), while for large τ ($>10^{-6}$ s), the statistical ratio of the yields of reactions (1) and (2), amounting to 1:3, is attained[55,65].

Table 9. The isotope composition of the hydrogen (H_2:HD:D_2) evolved in the photolysis of specimens I–IV at 77 K and after photolysis on heating the specimens to room temperature[55].

Specimen	Photolysis			Heating		
	H_2:HD:D_2	HD/H_2	HD/D_2	H_2:HD:D_2	HD/H_2	HD/D_2
I	72:16:12	0.22	1.3	69:19:12	0.28	1.6
II	82:9.6:8.4	0.12	1.1	64:22:14	0.34	1.6
III	73:7:20	0.096	0.35	74:9:14	0.12	0.53
IV	0:19:81	—	0.23	0:18:82	—	0.22

Notation: I—1:1 C_2H_4–C_2D_4 copolymer (irradiation with 147 nm light); II—1:1 C_2H_4–C_2D_4 copolymer (123.6 nm); III—1:1 polyethylene–deuteropolyethylene mixture (147 nm); IV—deuteropolyethylene (147 nm).

Thus at 77 K process (2) and the subsequent processes



take place on heating PE containing captured charges with $\tau \gg 10^{-6}$ s (with a probability of 0.75). The hydrogen evolved in the course of photolysis is formed via a non-ionic mechanism or via rapid ($\tau < 10^{-6}$ s) recombination of "close" charged pairs in process (1), which does not give rise to HD. The fraction of HD in this hydrogen is therefore reduced. This explanation is supported also by the finding that the increase of the HD content in the retained hydrogen is particularly high on photolysis by light at $\lambda = 123.6$ nm (10 eV), compared with photolysis at 147 nm (8.4 eV).

However, the authors of a later review[66] believe that the triplet states of alkanes can decompose also with elimination of molecular hydrogen. Indeed, it has been shown[67] that the formation of fairly excited triplet states of 1,2-diphenylethane entails, together with the elimination of atomic hydrogen, also the elimination of molecular hydrogen with a quantum yield of 10^{-2}. Unfortunately, the yield in the elimination of atomic hydrogen was not determined in the above studies, which precludes the determination of the relative probabilities of these two processes involving the formation of hydrogen from the triplet state. However, comparison of the yields of double bonds and radicals and also of the isotope composition of hydrogen (Table 3) in the photolysis of linear hydrocarbons and in their radiolysis shows that, whereas the yields of atomic and molecular hydrogen elimination reactions in radiolysis are approximately identical[17,57,68], the elimination of molecular hydrogen predominates in photolysis[17,43,56,57].

This difference is due to the fact that, as a consequence of prohibition rules, virtually only the singlet state is excited in photolysis, whereas in radiolysis, where the main active factor is secondary radicals with an energy below 100 eV, such prohibition rules are missing (particularly for resonance energies of the electrons) and triplet states should be formed with a high probability already in the primary process and also in the ion recombination process. On the basis of this comparison, one may claim that the dominant process in the decomposition of the electronically excited triplet state is the elimination of atomic hydrogen with formation of a free radical.

According to Raymonda and Simpson[22], the 147 nm light excites only C–C bond electrons in hydrocarbons. On this basis, Holroyd[20] suggests that the elimination of molecular hydrogen should be attributed to the excitation of the electrons of the above bonds. However, it has been assumed[32] that the ^1E_u state, produced by the excitation of the C–H bonding electron, is responsible for the elimination of molecular hydrogen.

The decrease of the yield of hydrogen with increasing branching of hydrocarbons (Tables 4 and 8) has been explained[17,24], on the one hand, by the decrease of the number of CH_2 and CH–CH groups (molecular hydrogen is eliminated from these groups[45]) and, on the other hand, by the more effective consumption of the absorbed energy in processes involving the dissociation of the C–C bond.

The observed increase of the yield of processes involving the dissociation of the C–C bond with increasing branching of compounds is due to the weakening of the C–C bond near the branching point (for example, in the case of polymers, which is indicated by the decrease of the heat of polymerisation of the corresponding monomers, which amounts to 92, 69, and 54.5 kJ mol^{-1} for PE, PP, and PIB respectively[69]). It is noteworthy that the high yield in the dissociation of the C–C bonds of polymers is believed[70] to be caused (according to theoretical calculations of adiabatic potential curves) by the low activation energy for this process in the excited state and the correlation between the yields of C–C bond dissociation processes involving polymers and the corresponding heats of polymerisation is justified if the adiabatic potential curve in the ground state for a given bond characterises the potential curve in the excited state.

According to calculations[70], such a correspondence obtains for PE and PIB. However, in the case of polytetrafluoroethylene (which undergoes degradation on radiolysis) a high heat of polymerisation (165 kJ mol^{-1}) corresponds to a low activation energy in the excited state[70]. Such weakening of the C–C bond is caused by steric strain in the ground and excited states as a consequence of the presence of side groups; it leads to a decrease of the dissociative lifetime for the C–C bond dissociation reaction (this is indicated by the decrease of the fluorescence quantum yield of alkanes with increase of the degree of branching—see Table 1 and Refs. 34 and 37) and hence to an increase of the yield of processes involving the dissociation of this bond.

It is noteworthy that the dissociation of the C–C bond is observed mainly near the branching point and in hydrocarbons containing methyl side groups the C–C bonds of the main chain are largely dissociated (in the PP and PIB polymers the yield of the bond branching reactions involving the main polymer chain is approximately ten times higher than the yield corresponding to the methyl side groups[17,24,57,60]). Apart from the features examined above, in PE, PI, and PIB there is an increase of the overall quantum yield of the photodecomposition of the polymers (Table 10). It has been noted[17,24] that, with increased degree of branching in the above series of compounds, the efficiency of the deactivation of the electronically excited states diminishes with a simultaneous increase of the contribution of processes involving the dissociation of the C–C bonds in the main polymer chain. On the basis of the results of studies[34–37] of the fluorescence of saturated hydrocarbons, this effect has been explained by the increase of the lifetime of the excited states with increase of the number of carbon atoms in linear alkanes (Table 1) accompanied by an increase of the fluorescence quantum yield. Therefore, on the basis of the data in Table 1 for PE, one may expect still higher lifetimes of the excited singlet states, which would promote their effective deactivation, particularly in the solid phase. Such increase of the lifetime of excited states has been explained[34–37] by the diminution of the changes in the internuclear distances in the excited state (as a consequence of the delocalisation of the electronic excitation over a long chain), which diminishes the probability of non-radiative transitions (for example, chemical processes). This explanation is confirmed by the finding that the first absorption transition of normal alkanes undergoes a bathochromic shift with increasing number of carbon atoms, while the energy of the fluorescence transition remains unaltered[34–37]. This is one of the possible causes[43] of the low quantum yield of the photodecomposition of PE compared with that observed in the photolysis of the lower linear alkanes, where the photodecomposition quantum yield is close to unity[1,32,38].

It has been established (see Table 1 and Refs. 35–37) that the luminescence quantum yield or branched alkanes is appreciably lower than for normal alkanes (by a factor of approximately 10). It is suggested that the emitting state is characterised by a high degree of localisation of the electronic excitation near the branching point. The localisation of the electronic excitation is accompanied by a large change in internuclear distances and this induces an increase of the rates of certain non-radiative processes, i.e. polymer chain degradation processes. Another possible explanation

involves a diminution of matrix effects hindering the photodecomposition of polymer molecules on transition to the amorphous PIB polymer[24].

Table 10. The quantum yields of the primary photolytic processes involving PE, PP, and PIB on irradiation with 147 nm light[17,24].

Process	PE	PP	PIB
Elimination of hydrogen molecule	~0.3	⩽0.25	⩽0.07
Degradation with formation of terminal double bonds	0.03	~0.25	0.8

It is interesting to compare certain predictions of the molecular exciton theory for σ-bonds of alkanes, examined in a number of studies[23,28–31], with the results of experiments on the photolysis of PE by 147 nm light. In the first place one should note that the light quantum with $\lambda = 147$ nm has an energy of 8.4 eV, which is apparently sufficient for the formation of an exciton (according to some data[23,28–31], the formation of an exciton requires an energy of ~7.5–9.5 eV). According to the above investigations[23,28–31], the excitation energy of linear alkanes can be divided into two parts, one of which is localised at the C–H bonds of the $\sim CH_2\sim$ group and the other migrates from one C–C bond to another. Only localised excitation of carbon–hydrogen bonds can lead to the formation of a hydrogen atom or an H_2 molecule as a result of their separation from the $\sim CH_2\sim$ group.

However, the results of experiments on the photolysis of PE conflict with this postulate of the theory of singlet σ-bond excitons. The results are as follows. An H_2 molecule is eliminated not only from a single carbon atom but also from two neighbouring atoms[45] and there is excitation energy transfer from deuterated units to the usual units on photolysis of the C_2D_4–C_2H_4 copolymer[45]; the double bonds formed on photolysis hinder the formation of hydrogen[17,57], the quantum yield of hydrogen increasing with temperature and approaching unity (see Table 8 and Refs. 43 and 44).

IV. PHOTOLYSIS OF HYDROCARBONS CONTAINING INDIVIDUAL DOUBLE BONDS

1. Optical Spectroscopy

Absorption by ethylene is observed at $\lambda \cong 200$ nm [71,72] (Fig. 4). At $\lambda \cong 175$ nm, a series of sharp intense peaks are observed and are superimposed on the absorption continuum with a maximum at ~164 nm. A new series of sharp bands are observed at ~142 nm and are superimposed on another continuum with maximum absorption at ~130 nm. It is believed to be established[71] that the long-wavelength absorption and the first continuum are due to the singlet excitation of the electron from the bonding molecular π orbital $1b_{2u}$ with transition to the antibonding π orbital $1b_{3g}$. The sharp absorption bands at 175 nm are due to Rydberg transitions; the lowest Rydberg transition $N \rightarrow 3s$ is observed at 174.4 nm. Rydberg transitions ($\pi \rightarrow 3p$, $\pi \rightarrow 3d$) [71] have also been noted in the range 154–118 nm. It is believed that the second absorption continuum of ethylene at 125 nm is due to the $\sigma \rightarrow \sigma^*$ transition. The ionisation of ethylene begins at 128 nm.[71] It has been suggested[71,73] that the ethylene molecule in the lowest Rydberg state has been "twisted" by an angle of 30° relative to the geometrical plane in the ground state. The geometry of the ethylene molecule in the singlet π^* state has not been established, while in the triplet state the molecule has been "twisted" by an angle of 90°.

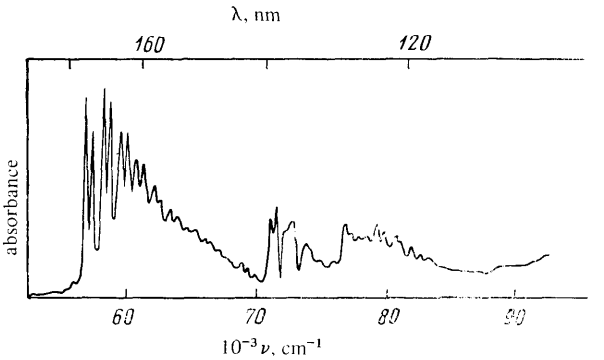


Figure 4. Absorption spectrum of gaseous ethylene in the vacuum ultraviolet region[72].

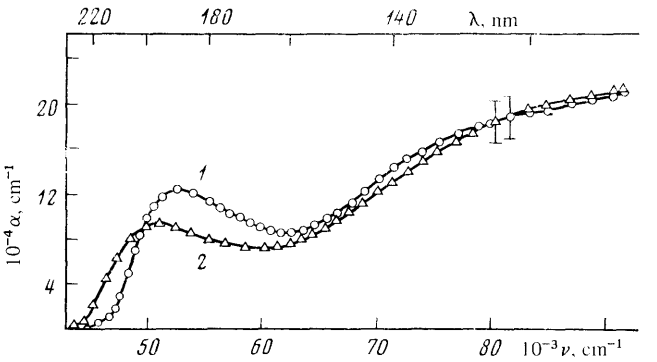


Figure 5. Absorption spectra: *1*) polybutadiene; *2*) polyisoprene[59]; α = decadic absorption coefficient.

As for ethylene, the first intense band in the absorption spectra of alkylolefins is due to the $\pi \rightarrow \pi^*$ transition and the fine structure superimposed on this band is less well resolved than for ethylene. It has been noted[71] that, with increase of the number of alkyl groups at the double bond, the absorption band undergoes a bathochromic shift (Fig. 5). The literature data on the oscillator strengths of various substances at the wavelength of the absorption band of carbon–carbon double bond ($\pi \rightarrow \pi^*$ transition) have been compiled in a monograph[71]. These data show that the oscillator strengths of compounds of different types are in the range from 0.26 to 0.59.

The fluorescence of mono-olefins irradiated with light corresponding to the absorption band of the double bonds has been studied[37,73]. On excitation by 184.9 nm light, a weak emission by gases at a pressure of 1 atm is observed (propene has a fluorescence band maximum at $\lambda_f \cong 223$ nm and *cis*- and *trans*-but-2-enes have $\lambda_f \cong 223$–227 nm). The fluorescence quantum yields for these substances are $\sim(1-2) \times 10^{-6}$. A similar luminescence has been observed also for pure liquids: hex-1-ene ($\lambda_f \cong 236$ nm), *cis*-hex-2-ene ($\lambda_f \cong 238$ nm), and *trans*-hex-2-ene ($\lambda_f \cong 235$ nm). The luminescence quantum yields for these substances are $(5-7) \times 10^{-6}$. With increase of the degree of branching, the fluorescence undergoes a bathochromic shift and its quantum yield increases[37,73]. Thus the fluorescence of liquid tetramethylethylene is observed at $\lambda_f \cong 258$ nm with a quantum yield of 1.5×10^{-4}.

2. Photolysis of Mono-olefins

The photolysis of ethylene has been studied in greatest detail. For photons with energies ranging from 6.1 to 11.8 eV, the elimination of H_2 is the main process[38,74,75] [$\Phi(H_2) \cong 0.45 \pm 0.05$ in the range of photon energies 8.4–6.4 eV [38,74]]. Experiments on the photolysis of CH_2CD_2 by 147 and 123.6 nm light have shown[38] that the elimination of H_2 and D_2 from a single carbon atom is more probable than the elimination of HD from two carbon atoms. Furthermore, it has been established that the relative probabilities of the formation of H_2, D_2, and HD are independent, within the limits of experimental error, of the wavelength and the phase state of ethylene[76]. However, it has been stated that the probability of the competing process

$$C_2H_4 + h\nu \rightarrow \overset{*}{C}_2H_3\,(C_2H_2 + \dot{H}) + \dot{H}$$

increases with increase of the photon energy from 8.4 to 11.6–11.8 eV. In addition the following process has also been observed:

$$C_2H_4 + h\nu \rightarrow 2\ddot{C}H_2 \quad .$$

It has been suggested that there should be at least three different electronic states of ethylene in order to account for the photodecomposition processes in the range of photon energies from 6.4 to 8.4 eV.

The photolysis of ethylene by 104.8–106.7 nm light[38,77] entails ionisation and the formation of superexcited states:

$$C_2H_4 + h\nu \begin{cases} \rightarrow (C_2H_4^{\neq})^+ + e^- \\ \rightarrow C_2H_4^{**} \rightarrow (C_2H_4^{\neq})^+ + e^- \end{cases} .$$

The superexcited ethylene molecule ($C_2H_4^{**}$) can also decompose in the following processes:

$$C_2H_4^{**} \begin{cases} \rightarrow C_2H_2 + H_2 \\ \rightarrow C_2H_2 + 2\dot{H} \end{cases} .$$

It is believed[77] that, on collision with an ethylene molecule, $C_2H_4^+$ gives rise to a vibrationally excited ion:

$$C_2H_4^+ + C_2H_4 \rightarrow (C_4H_8^{\neq})^+ \quad .$$

In the absence of deactivating collisions, the $(C_4H_8^{\neq})^+$ ion decomposes:

$$(C_4H_8^{\neq})^+ \begin{cases} \rightarrow C_3H_5^+ + \dot{C}H_3 \\ \rightarrow C_4H_7^+ + \dot{H} \end{cases} .$$

Ethylene has been photolysed[76] in the condensed phase at 20 K by photons with energies from 8.4 to 21.2 eV. It has been established that, for higher photon energies, the relative yields of the products are comparable to the yields in the decomposition of solid ethylene. The relative yields of acetylene and cyclobutane (these are not the main products in the photolysis by photons with an energy of 8.4 eV) increase by an order of magnitude for higher photon energies, where the ions play a significant role.

Table 11. The composition of the products of the gas-phase photolysis of propene[78].

Product	147 nm	123.6 nm	Product	147 nm	123.6 nm
Hydrogen	7.6	14.7	Allene	7.4	6.8
Methane	3.4	3.8	Isobutane	11.4	8.6
Acetylene	38.0	34.9	Isobutene + but-1-ene	3.5	4.8
Ethylene	12.2	18.2	*trans*-But-2-ene	7.2	4.8
Ethane	7.4	4.1	*cis*-But-2-ene	1.9	0.0

The products of the photolysis of propene by 147 and 123.6 nm light are presented in Table 11.[78,79] The hydrogen formed in the photolysis is split off mainly in molecular processes:

$$CH_3CH{=}CD_2^{\neq} \begin{cases} \rightarrow H_2 + \ddot{C}HCH{=}CD_2 \\ \rightarrow H_2 + CH_2{=}C{=}CD_2 \end{cases} .$$

Acetylene is formed as a result of the rapid consecutive dissociation of two bonds:

$$CH_3CH{=}CH_2 \rightarrow \dot{C}H_3 + \dot{C}H{=}CH_2^{\neq} \quad ,$$

$$\dot{C}H{=}CH_2^{\neq} \rightarrow CH{\equiv}CH + \dot{H} \quad .$$

In the photolysis of the $C_3H_6 + C_3D_6$ mixture the yield of C_2H_4 is higher than that of C_2D_3H. Hence it follows that ethylene is partly formed via a molecular pathway:

$$CH_3CH{=}CH_2 + h\nu \rightarrow \ddot{C}H_2 + CH_2{=}CH_2 \quad .$$

Another process is also possible:

$$\dot{H} + C_3H_6 \rightarrow \dot{C}_3H_7 \rightarrow \dot{C}H_3 + C_2H_4 \quad .$$

The photolysis of propene by 123.6 nm light entails ionisation with a quantum yield of 0.197. Direct ionisation and self-ionisation in the superexcited state are observed. The $C_3H_6^+$ ions formed are involved in ion–molecule reactions:

$$C_3H_6^+ + C_3H_6 \rightarrow C_6H_{12}^+ \quad ,$$

$$C_6H_{12}^+ + C_3H_6 \rightarrow C_6H_{10}^+ + C_3H_8 \quad .$$

The process

$$C_6H_{12}^+ + C_6H_6 \rightarrow C_9H_{18}^+ ,$$

is possible but with a much lower probability.

In the photolysis of but-1-ene by 184.9, 147, 123.6, and 104.8–106.7 nm light, the main products are formed on fragmentation of the excited molecule[80]. Allene, buta-1,3- and buta-1,2-dienes, ethylene, and acetylene are formed (Table 12). When a hydrogen atom interacts with a double bond, the butyl radical is formed. On photolysis of trimethylethylene by 147 and 123.6 nm light, the following main products are formed: isopropene, buta-1,3-diene, propyne, allene, and ethylene[81] (Table 13).

It follows from Tables 12 and 13 and the results of a series of investigations[80–97] that, in the photolysis of linear olefins by light corresponding to the absorption band of double

bonds, the main process is the dissociation of the C–C β-bond if such is present and a C–H bond if there is no C–C bond in the β-position:

$$C_4H_8\text{-}1 + h\nu \xrightarrow{\Phi=0.71} \dot{C}H_3 + \dot{C}H_2{-}CH{=}CH_2 \ ,$$

$$C_4H_8\text{-}2 + h\nu \xrightarrow{\Phi=0.6} \dot{H} + \dot{C}H_2{-}CH{=}CH{-}CH_3 \ .$$

Analogous processes occur also in the photolysis of hex-2-ene and but-2-ene by 202.6 and 206.2 nm light:

$$C_6H_{12}\text{-}2 + h\nu \rightarrow CH_3CH{=}CH\dot{C}H_2 + \dot{C}H_2CH_3 \ ,$$

$$C_4H_8\text{-}2 + h\nu \rightarrow CH_3CH{=}CH{-}\dot{C}H_2 + \dot{H} \ .$$

In branched olefins the methyl side groups promote the dissociation of the C–C bonds in the α-position:

$$iso\text{-}C_4H_8 + h\nu \rightarrow \begin{cases} \xrightarrow{\Phi\geq 0.78} CH_3{-}\dot{C}{=}CH_2 + \dot{C}H_3 \\ \xrightarrow{\Phi\geq 0.25} \dot{C}H_2{-}C{=}CH_2 + \dot{H} \\ \qquad\quad | \\ \qquad\quad CH_3 \end{cases} .$$

Table 12. The quantum yields of the primary processes in the decomposition of the excited state of but-1-ene (C_4H_8-1) in photolysis by light corresponding to the intrinsic absorption band[80].

Product	184.9 nm	147 nm	123.6 nm	104.8–106.7 nm
$C_3H_4+\dot{C}H_3+\dot{H}(CH_4)$	0.04	0.38	0.23	0.16
$C_4H_6+2\dot{H}(H_2)$	—	0.32	0.36	0.17
$2C_2H_4$	0.09	0.04	0.05	0.2
$\dot{C}_2H_3+C_2H_5+\dot{H}$	—	0.04	0.05	
$C_2H_2+\dot{C}_2H_5+\dot{H}$	—	0.16	0.12	
$C_2H_2+C_2H_6$	0.1	0.03	0.02	0.33
$C_2H_2+2\dot{C}H_3$	—	0.04	0.05	
$C_3H_6+\dot{C}H_2$	—	0.03	0.04	0.05
$\dot{C}_4H_7+\dot{H}$	0.12	≤0.05	≤0.05	≤0.05
$\dot{C}_3H_5+\dot{C}H_3$	0.71	0.0	0.0	0.0

Table 13. The quantum yields of the decomposition processes involving the excited state of the trimethylethylene (C_5H_{10}) molecule[81].

Product	147 nm	123.6 nm	Product	147 nm	123.6 nm
$\dot{C}_5H_8+2\dot{H}(H_2)$	0.33	0.28	$[C_5H_{10}^+]^* + e^-$	0.00	0.22
$C_3H_4+2\dot{C}H_3$	0.27	0.2	$\dot{C}_5H_9+\dot{H}$	0.15	0.12
$C_4H_6+\dot{C}H_3+\dot{H}(CH_4)$	0.15	0.1	Other products	0.09	0.08

In the photolysis by light at $\lambda \leq 145$–150 nm decomposition processes involving the formation of three species, namely a hydrogen molecule and two radical species ($\dot{H}$ and the hydrocarbon radical or $2\dot{H}$), begin to predominate. A decrease of the yields of certain products with increase of pressure has been noted in the photolysis of olefins by light corresponding to the absorption band of double bonds[81,84,85,89,90,93,96]. The influence of pressure is due to the following sequence of processes:

$$M + h\nu \rightarrow M^{**} \ ,$$

$$M^{**} \rightarrow R^* + R_1 \ ,$$

$$R^* \rightarrow m + \dot{H} \text{ (or } \dot{C}H_3) \ ,$$

where m is a molecule containing an acetylenic or cumulated bond[84,93,94]. The influence of pressure is due to the stabilisation of the excited radical R* in the process

$$R^* + M \rightarrow R + M \ .$$

A similar mechanism of the effect of pressure has been considered also in the photolysis of hex-2-ene and but-2-ene by 202.6 and 206.2 nm light[92]:

$$C_6H_{12}\text{-}2 + h\nu \rightarrow C_6H_{12}\text{-}2^{**} \ ,$$

$$C_6H_{12}\text{-}2^{**} \rightarrow C_6H_{12}\text{-}1^{**} \ ,$$

$$C_6H_{12}\text{-}2^{**} \rightarrow C_6H_{12}\text{-}2^* \ ,$$

$$C_6H_{12}\text{-}2^{**} \rightarrow CH_3CH{=}CH\dot{C}H_2 + \dot{C}H_2CH_3 \ ,$$

$$C_6H_{12}\text{-}2^* + M \rightarrow C_6H_{12}\text{-}2 + M \ .$$

The absence of an influence of pressure on the yields of various products in photolysis by short-wavelength light has been explained[88] by the faster decomposition of excited radicals and molecules owing to their higher excess energy. The photolysis of olefins by 123.6 and 104.8–106.7 nm light involves the ionisation of double bonds with a quantum yield of ~0.2–0.3.[81,87,88,97]. The ions formed participate in ion-molecule reactions leading to the formation of saturated hydrocarbons as well as hydrocarbons containing a larger number of carbon atoms than the initial olefin.

3. Photolysis of Diene Polymers

Polybutadiene (PB) and polyisoprene (PI). The photolysis of polymers containing individual double bonds (PB and PI) on irradiation with 147 and 123.6 nm light has been investigated[17,56,59,98]. It has been established that the main processes involve the consumption of double bonds and their *cis–trans* isomerisation. In addition, hydrogen and intermolecular cross-links are produced (Table 14) as well as unidentified hydrocarbon products. The formation of these hydrocarbons entails a decrease of the thickness of PB and PI film by 30–50 nm on photolysis by 147 and 123.6 nm light with a dose of $(1–2) \times 10^{18}$ quanta cm^{-2}. It is believed that mainly electronically excited states of the polymer molecules arise in this instance as in the photolysis of olefins in the gas phase:

$$M + h\nu \rightarrow M^* \ .$$

The decomposition of M* involves the elimination of atomic hydrogen:

$$M^* \rightarrow R + \dot{H} \ .$$

However, the photolysis of PB and PI differs significantly from the photolysis of olefins in the gas phase by the fact that the overall yield of diene, cumulated, and acetylenic bonds (~0.06) is approximately ten times lower than in the gas-phase photolysis of butenes and pentenes, where the yield of the above bonds is ~0.5.[80,81,87,94]. The difference is believed[17,59] to be caused by the transition to the condensed phase, which suppresses the secondary decomposition reactions of the excited radicals leading to the formation of these bonds:

$$M^* \rightarrow \begin{cases} R^* + \dot{C}H_2{-}CH{=}CH{\sim} \\ m + \dot{H} \end{cases} .$$

The hydrogen detected is formed in the molecular elimination reaction

$$M^* \begin{cases} \rightarrow H_2 + \sim CH{=}CH{-}CH{=}CH{-}CH{=}CH \sim \\ \rightarrow H_2 + \sim CH{=}C{=}CH{-}CH_2 \sim \end{cases} .$$

C–C bond dissociation reactions involving the main polymer chain take place:

$$M^* \begin{cases} \rightarrow \sim CH{=}CH{-}\dot{C}H_2 + \dot{C}H_2{-}CH{=}CH \sim & (3) \\ \rightarrow \sim CH{=}\dot{C}H + \dot{C}H_2{-}CH_2{-}CH{=}CH \sim . & (4) \end{cases}$$

It is believed[17,59] that the probability of process (3) is higher than that of process (4) owing to the fact that the C–C bond in the β-position is weaker (~231 kJ mol^{-1}). The strength of this bond is appreciably lower than that of the usual C–C bond (~374 kJ mol^{-1}) owing to the resonance stabilisation of the two allyl radicals formed on dissociation of the main polymer chain[99].

It is thought possible that the double bond migrates with formation of a conjugated diene double bond[59]:

$$M + h\nu \rightarrow \sim CH{=}CH{-}CH_2{-}CH{=}CH \sim + h\nu \rightarrow \sim CH{=}CH{-}CH{=}CH \sim .$$

The primary process can also be the formation of cyclopropane groups:

$$M + h\nu \rightarrow \sim CH_2{-}\dot{C}H{-}\dot{C}H{-}CH_2 \sim \rightarrow \sim CH_2{-}\dot{C}H{-}CH_2{-}\dot{C}H_2 \sim \rightarrow \quad (5)$$
$$\rightarrow \sim CH_2{-}CH(\diagup\diagdown CH_2){-}CH \sim .$$

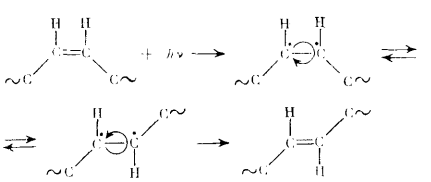
This process occurs in the photolysis of PB and PI by 253.7 nm light, assumed to proceed via the triplet state[98,100], and in the triplet sensitisation of but-1-ene in the gas phase by mercury atoms[15]. Cyclopropane groups can also be formed in the isomerisation of the allyl radical:

$$\sim CH_2{-}CH{=}CH{-}\dot{C}H_2 \rightarrow \sim CH_2{-}CH(\diagup\diagdown CH_2){-}\dot{C}H \quad . \quad (6)$$

Cross-links are formed mainly in radical recombination processes and possibly also in the interaction of radicals with double bonds:

$$R + \sim CH{=}CH \sim \rightarrow \text{cross-link} + R'.$$

It has been established[98] that *cis–trans* isomerisation takes place in the photolysis of PB by 123.6 nm light. It has been suggested that this process proceeds as follows: when a light quantum is absorbed, the π-electrons are transferred to the antibonding orbital, whereupon there is a possibility of free rotation leading to a change in the steric configuration[99]:



A similar process should apparently be observed also in photolysis by light at 147 nm, since it has been noted[100] that *cis–trans* isomerisation proceeds also in the photolysis of PB and PI by light at λ = 253.7 nm with a quantum yield of ~0.04.

The difference between the yields of reactions involving the consumption of double bonds in photolysis by 147 and 123.6 nm light is striking (Table 14). It is believed to be caused by the ionisation of double bonds by 123.6 nm light, in contrast to 147 nm irradiation. The ion–molecule mechanism of the cross-linking of PB and PI in photolysis by light at λ = 123.6 nm has been considered:

$$M + h\nu \rightarrow \sim CH_2{-}\dot{C}H{-}\overset{+}{C}H \sim + e^-,$$
$$\sim \dot{C}H{-}\overset{+}{C}H \sim + M \rightarrow \sim CH_2{-}\overset{+}{C}H \sim + R ,$$
$$\sim CH_2{-}\overset{+}{C}H \sim + \sim CH{=}CH \sim \rightarrow \sim CH_2{-}CH(\overset{+}{C}H){-}CH \sim .$$

This is followed by further chain propagation.

Table 14. The quantum yields of the main processes in the photolysis of polybutadiene and polyisoprene on irradiation with 147 and 123.6 nm light.

Process	Polybutadiene		Polyisoprene	
	147 nm	123.6 nm	147 nm	123.6 nm
Consumption of individual double bonds	0.28 [59]	1.3 [59]; 1.53 [98]	0.24 [59]	1.3 [59]
cis–trans-Isomerisation	—	0.25 [98]	—	—
Formation of H_2	0.019 [59]	0.023 [59]	0.015 [59]	0.022 [59]
Formation of intermolecular cross-links	0.012–0.024 [56]	0.027–0.056 [56]	0.008–0.03 [56]	0.048–0.063 [56]

Note. The numbers in square brackets denote references (Ed.of Translation).

It has been postulated[56] that the free-radical mechanism of cross-linking determines the formation of a gel in photolysis by 147 nm light, while in photolysis by 123.6 nm light the ion–molecule cross-linking mechanism should play a decisive role. The large difference between the yields of the cross-linking and double bond consumption reactions is striking, although, according to both the free-radical and ion–molecule mechanisms, these quantities should be similar. The higher overall quantum yield (>1)† (Table 13) in photolysis by 123.6 nm light indicates a chain mechanism of the destruction of double bonds.

The yields of the cross-linking reaction are much lower than these values, which makes it necessary to seek additional double bond destruction processes apart from intermolecular cross-linking. It has been suggested[17,56,59] that there exist two types of such processes: intermolecular cross-linking with formation of cyclopropane groups [processes (5) and (6)] and the formation of multiple intermolecular cross-links in the same pair of macromolecules, which should be promoted by chain processes due to the migration of a charge or a radical. The ratio of the rates of these processes and the number of cross-links in the pair of macromolecules probably depend on the type of active radiation: on passing from photolysis by 147 nm light to photolysis by 123.6 nm light, the yield of the double bond consumption reaction increases by a factor of 5–6 and the yields of the cross-linking reactions increase only by a factor of two.

V. PHOTOCHEMICAL REACTIONS OF CERTAIN POLYMERS INVOLVING OXYGEN

The influence of vacuum ultraviolet light in the wavelength range ~110–220 nm on polymers in the presence of oxygen has been investigated in several studies[101–104].

†Probably >0.1 (Ed.of Translation).

Thus a silicone rubber, poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA) have been irradiated with the light of a hydrogen discharge[102]. During photolysis by radiation *in vacuo* in the course of approximately 100 h, no changes in the irradiated films were detected by infrared spectroscopy. However, during photolysis the films changed colour, particularly the PVC films, and ceased to dissolve in solvents, which indicates the formation of intermolecular cross-links. After the addition of small amounts of oxygen to the photochemical cuvette, the absorption band due to carbonyl groups appeared in the infrared spectra.

PVC, PMMA, polystyrene (PS), and polycarbonate (PC) films 100–150 nm thick have been irradiated with light at λ = 110–200 nm in an atmosphere of nitrogen[101]. It was established that, on irradiation, the optical densities of the PVC and PMMA specimens decrease fairly appreciably in the first 15 min and then, having attained ~50% of the initial value, no longer change. The optical densities of PS and PC change very insignificantly during irradiation for 1.5 h. The irradiated sections of all four polymers become insoluble in solvents which are effective for the initial non-cross-linked polymers.

Table 15. Some parameters of the decomposition of polymers [rate of decomposition v (nm min^{-1}), quantum yield Φ, and consumption of O_2 molecules in the decomposition of one unit n] on irradiation with light at $\lambda \cong$ 100–200 nm in an atmosphere of oxygen[103].

Polymer	v, nm min^{-1}	Φ	n
PVC	16	0.32	1
PMMA	10	0.24	1
PS	1.6	0.01	10
PC	1.5	0.005	20
PTFE	2.5	0.1	2

The kinetics of the decomposition of polymer films by light at 110–200 nm have been investigated[101,103] in an oxygen-containing medium. Table 15 presents the results of measurements of the rates of decomposition of PVC, PMMA, PS, PC, and polytetrafluoroethylene (PTFE). The following stable decomposition products of PVC, PMMA, PS, and PC were detected: CO_2, CO, and H_2O. A more involved mass spectrum containing the following ions was obtained for PTFE: F^+, CO^+, CO_2^+, COF^+, COF_2^+, CF_3^+, $C_2F_4^+$, $C_2F_5^+$, and $C_2F_4O_2^+$; other ions with a mass number m/e > 180 were also detected. The absence of a signal due to fragments resulting from the decomposition of the polymer chain in the mass spectra of polymers without fluorine and the low consumption of oxygen are apparently due to the activity of the decomposition products of these polymers: they settle on the walls of the reactor in the form of solid deposits. It has been suggested that the stable radicals $\sim CF_2CF(\dot{O}_2)CF_2\sim$ and $\sim CF_2CF_2\dot{O}_2$ participate in the PTFE decomposition reactions. The formation of such radicals on irradiation of PTFE with vacuum ultraviolet light (~120–160 nm) with subsequent exposure of the specimen to air has been detected by EPR.[104] The authors[104] believe that the peroxy-radicals detected are formed from central ($\sim CF_2\dot{C}FCF_2\sim$) and terminal ($\sim CF_2-\dot{C}F_2$) radicals under the influence of vacuum ultraviolet light.

VI. CONCLUSION

Thus the photolysis of two classes of hydrocarbons (including polymers) by vacuum ultraviolet radiation, mainly in the wavelength range 105–200 nm, results in the formation of electronically excited states due to the transitions $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$, Rydberg states are excited, and ionisation takes place.

In the photolysis of the compounds examined, both molecular and free-radical products can be formed in the photochemical process. The formation of primary products in an excited state is characteristic of olefins, which can lead to their subsequent dissociation in secondary processes. It has been noted for a number of substances that secondary fragmentation can be suppressed by increasing the pressure in the gas phase, by conversion into the liquid phase, and particularly by conversion into the condensed phase (polymers). A decrease of the yield of primary processes has also been noted for PE owing to the transition to the condensed phase and the formation of long-chain molecules.

Comparison of primary processes involving low-molecular-weight substances in the gas phase and polymers with a similar structure in the condensed phase shows that the primary processes are as a rule the same in both cases. This makes it possible to predict the photochemical processes in polymers on the basis of the results of the photolysis of low-molecular-weight substances in the gas phase. However, the analogy is not complete. Thus PIB gives rise to the formation of conjugated diene double bonds, which has not been noted for low-molecular-weight branched alkanes. This feature is apparently due to the regularity of the structure of the PIB macromolecules.

It is of interest to compare certain characteristics of the photolysis of polymers by vacuum ultraviolet light, i.e. by light corresponding to the intrinsic absorption band, and light at $\lambda \gtrsim 200$ nm, when absorption is due to impurities or anomalies in the structure of the real macromolecule. In photolysis by light at $\lambda \lesssim 200$ nm the quantum yields of products derived from the polymers investigated are in the range ~0.1–1, while in the photolysis of the same polymers by light at $\lambda \gtrsim 200$ nm the quantum yields are lower by a factor greater than ten[99]. Whereas the photolysis of PE, PP, and PBI by vacuum ultraviolet radiation involves the occurrence of molecular processes, in photolysis by light at $\lambda \gtrsim 200$ nm free-radical processes take place. Since the absorption coefficients of polymers in the vacuum ultraviolet region are high (~10^3–10^6 cm^{-1}), the photochemical reactions take place under the influence of this light in a thin surface layer (~0.1–100 μm) and the energy absorbed in this layer is high, which leads to high degrees of conversion. As a result of this, a non-trivial phenomenon has been observed for a series of polymers (PP, PIB, PB, and PI): photo-etching of the surface layer, particularly in the presence of oxygen.

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Catalytic Oxidation of Propene

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The oxidation of propene on simple and mixed oxide catalysts to form various oxygen-containing products—acrylaldehyde, acrylic acid, acetone, and acetic acid—is surveyed, and the role of individual components of the active catalysts discussed. A list of 110 references is included.

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I. INTRODUCTION

Catalytic oxidation of propene is one of the chief methods for obtaining monomers and intermediates in organic synthesis. The increasing demands made by the national economy for such important compounds as aldehydes, ketones, and carboxylic acids require the development of new, more economic methods for their production. A problem of primary importance is to choose active and highly selective catalysts. Those containing molybdenum have become the most widely used mixed oxide catalysts for the selective oxidation of propene.

A vast literature has now accumulated on the catalytic oxidation of propene to acrylaldehyde. The kinetics has been studied in detail, reliable data are available on the mechanism of the formation of acrylaldehyde on several catalysts, and highly effective industrial catalysts have been developed.

Studies of the oxidation of propene to acrylic and acetic acids, acetone, and methyloxiran have increased during recent years. The production of acrylic acid has now reached the stage of semi-industrial trials, that of acetone and acetic acid is at the level of laboratory investigation, and an active catalyst is being sought to obtain methyloxiran.

There have been hardly any reports of processes in which such oxygen-containing compounds as propionaldehyde, propionic acid, formaldehyde, formic acid, and acetaldehyde are formed as main products. These compounds are usually obtained as by-products in various processes involving the oxidation of propene.

II. OXIDATION OF PROPENE TO ACRYLALDEHYDE AND ACRYLIC ACID

Among individual oxides copper(I) oxide is the most active catalyst for the oxidation of propene to acrylaldehyde[1]. This process has been developed to an industrial level, but the use of bismuth molybdate has enabled higher indices to be achieved and also research on the preparation of mixed oxide systems containing molybdenum to be started.

In 1978 Keulks published a review[2] which touched only part of the problem, with the oxidation of propene mainly on bismuth molybdates as example. Reference 3 also reviews the physicochemical and catalytic properties of the latter products, and includes structural features and data on the kinetics and the mechanism of the oxidation of propene. The present Review attempts to summarise the disconnected data published during recent years on the oxidation of propene.

It can be accepted as established that bismuth molybdate Bi_2MoO_6 is almost inactive[4]. It comprises octahedra of oxygen atoms surrounding a molybdenum ion and alternating with layers of bismuth ions. The structures of the molybdates $Bi_2Mo_2O_9$ and $Bi_2Mo_3O_{12}$ have been less thoroughly studied, but they definitely contain more oxygen vacancies than in Bi_2MoO_6. Among the bismuth molybdates $Bi_2Mo_3O_{12}$ possesses moderate activity, while $Bi_2Mo_2O_9$ and the two-phase catalysts (mixtures of Bi_2MoO_6 and $Bi_2Mo_3O_{12}$) have about the same high activity. X-Ray electron spectroscopy has shown that in the catalysts Bi_2MoO_6, $Bi_2Mo_2O_9$, and $Bi_2Mo_3O_{12}$ the ratios of bismuth to molybdenum are about the same on the surface and in the mass[4]. In two-phase specimens in which the mass ratio is 1–2 : 1 the surface ratio is unity; it gradually decreases with increase in the molybdenum content, and very slowly increases with increase in the bismuth content. The catalytic activity is assumed to be determined by a surface phase having the ratio Bi : Mo $\approx$ 1. One factor determining the activity and the selectivity of bismuth molybdates is the high rate of diffusion of oxygen in the crystal lattice.

Using ^{18}O and $CD_3.CD{:}CH_2$ as labelled reagents Keulks et al. have established[5] that on the bismuth molybdates $Bi_2Mo_3O_{12}$ and Bi_2MoO_6 acrylaldehyde is formed solely by a redox mechanism, and that the reaction involves oxygen from several surface layers of the lattice (respectively 13–47 and 79–280 monolayers). Oxidation of acrylaldehyde to carbon dioxide is effected also by oxygen of the crystal lattice.

The activation energy of removal of oxygen ions O^{2-} located between layers of molybdenum and bismuth atoms is much lower for those attached to molybdenum[6,7]. Hence experimental results are regarded[6,7] as indicating that on selective oxidation the adsorbed hydrocarbon interacts with an oxygen ion attached to bismuth, and are explained by the formation of oxygen vacancies in the molybdenum layer during preliminary reduction of the bismuth–molybdenum oxide catalyst; vacancies formed at bismuth(III) ions are filled by oxygen ions attached to molybdenum(VI), while oxygen from the gas phase fills vacancies at the molybdenum ions. Such a mechanism of migration of oxygen ions ensures a steady state of oxidation of the catalyst and explains the enhanced activity and the selectivity of bismuth molybdates in comparison with the individual oxides.

The structure of bismuth molybdate and the energy of bonding of oxygen in the lattice are influenced by the introduction of various additives. Heavy oxygen $^{18}O_2$ has been used as tracer to study the selectivity of the oxidation of propene to acrylaldehyde on bismuth molybdate modified with cobalt, nickel, manganese, magnesium, strontium, barium, and lead[8]. Since the acrylaldehyde and carbon

dioxide had the same oxygen-18 content, but the water a diminished content, it was supposed that two types of oxygen atoms—active towards addition to propene and active towards removal of hydrogen atoms—were present in the catalyst. After addition of cobalt, nickel, manganese, or magnesium the catalyst has the α-$MnMoO_4$ structure and the selectivity of oxidation of propene to acrylaldehyde reaches 93–97%, whereas a catalyst containing strontium, lead, or barium gives a lower selectivity (71–87%) and has the scheelite structure. The varying reactivity of oxygen in the lattice is governed by the modifying effect of the additives.

Introduction of small quantities (0.2 mass %) of phosphorus into bismuth molybdate $Bi_2Mo_3O_{12}$ transforms it into $Bi_2Mo_2O_9$. When the phosphorus content exceeds 1.3 mass %, a ternary chemical compound $2Bi_2O_3.MoO_3.P_2O_5$ is formed[1]. A ternary compound has been observed also in the bismuth–molybdenum–iron system[9–11]. Addition of iron(III) is assumed to result in filling of cationic vacancies in $Bi_2Mo_3O_{12}$ and in formation of at least two ternary compounds having the proportions Pi : Fe : Mo = 1 : 1 : 1 and 3 : 1 : 2. It appears that Bi^{3+} and Fe^{3+} ions can be interchanged in these compounds without significant structural changes. The catalytic activity of bismuth–molybdenum–phosphorus and bismuth–molybdenum–iron oxide systems is attributed to the presence of ternary compounds.

Tracer and spectroscopic methods have been widely used[12–16] to investigate the mechanism of the partial oxidation of propene on bismuth–molybdenum and copper oxide catalysts. Experiments with deuterated propene have proved that the rate-determining stage in the formation of acrylaldehyde is detachment of a hydrogen atom from the methyl group.

Considerably more by-products (e.g. carbon dioxide, acetaldehyde are formed on the interaction of allyl radicals (obtained by the thermal decomposition of azo-3,3′-propene) on the surfaces of molybdenum(VI) and bismuth(III) oxides and on bismuth molybdates than in the conversion of propene or allyl iodide under corresponding conditions[17]. The hypothesis was therefore put forward that the oxidation of propene does not involve formation of a free allyl radical. These results together with experiments on the oxidation of allyl alcohol suggested[18] a mechanism of selective oxidation of propene with transition from π-allyl to σ-allyl molybdate before detachment of the second hydrogen atom with formation of acrylaldehyde and a reduced form of the catalyst.

Comparison of the products formed in the oxidation of propene on bismuth oxide and on bismuth molybdates indicates[19–21] that dissociative adsorption of propene with detachment of the first hydrogen atom takes place on a bismuth cation, while the role of molybdenum is merely to change the energy of bonding of oxygen with the catalyst.

The opposite view is also widely represented in the literature, that an allyl complex is formed on a multivalent molybdenum ion[22–30]. The alkene interacts with an oxygen vacancy in the vicinity of a molybdenum ion and forms a π-allyl complex of molybdenum, which is then oxidised by oxygen of the catalyst to the reaction products. The role of bismuth is merely to facilitate dehydration of and to reduce the catalyst surface.

The oxidation of propene and of acrylaldehyde to acrylic acid has been studied on the tellurium–molybdenum oxide system containing various additives[31]. The sequence of the latter with respect to selectivity of such oxidation is respectively

V>Mn>Sn>Ti>W>Ni>Cr>Bi>Co>Fe>Cu,

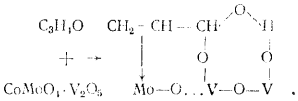
and the somewhat modified

V>Sn>Ti>Co>W>Cr>Bi>Ni>Fe>Cu>Mn.

The optimum catalyst for the oxidation of both compounds to acrylic acid is a tellurium–molybdenum oxide system containing 25 mass % of vanadium. The parallelism in the variation of catalytic properties with the vanadium content suggests that the oxidation of propene to acrylaldehyde and to acrylic acid takes place on the same active centres of the catalyst. The yield of acrylaldehyde and acrylic acid is increased significantly by the introduction of tellurium into the chromium–molybdenum oxide system[32]. Study of the acidity of the surface and of the surface complexes formed on adsorption of alkenes indicates that both carbon dioxide and acrylic acid result from the breakdown of carboxylate complexes formed on aprotic acid centres. The presence on the surface of proton-donor centres and the absence of active, weakly bound oxygen favour the formation of acids.

The catalytic properties of the cobalt–molybdenum oxide system, which is active in the oxidation of propene to acrylic acid, are significantly determined by the phase constitution. Maximum yield of the acid corresponds to the highest content of the acitve phase b-$CoMoO_4$.† Formation of the active phase is largely determined by the conditions of preparation of the specimens (pH, temperature of precipitation, concentrations of initial salt solutions, temperature of ignition).[33,34] Introduction of bismuth, chromium, and iron oxides into cobalt molybdate changes the content of the active phase and influences the selectivity of oxidation of propene to acrylaldehyde[34].

The introduction of vanadium and copper ions into cobalt molybdate increases the rate of formation of acrylic acid from acrylaldehyde by factors of 40 and 28 respectively. Nickel has the least effect[29]. It is significant that these additives lower the rate of conversion of propene into acrylaldehyde. It was suggested that they block the molybdate anions responsible for the formation of π-allyl complexes in molybdates. Electron spin resonance spectroscopy has shown that interaction of the catalyst with propene and with acrylaldehyde changes the oxidation states of the molybdenum ions and also of the additives; in particular, when the surface is modified with vanadium ions, reduced centres V^{4+} and V^{3+} are readily formed, and govern the oxidation-state transitions. Complex formation between acrylaldehyde and surface ions of the catalyst may involve interaction with both ethylenic and carbonyl bonds. Since the rate of conversion of acrylaldehyde into acrylic acid far exceeds the rate of oxidation of propene in the same direction, it was supposed[29] that in the case of acrylaldehyde interaction is effected at the carbonyl bond, with oxidation on cobalt molybdate containing added vanadium following the scheme



Catalytic activity is enhanced by the addition of tellurium and phosphorus to the cobalt–molybdenum oxide system: the conversion of propene reaches 80%, and selectivity with respect to acrylic acid and acrylaldehyde respectively 50% and 20%.[35] Investigation of the phase constitution of the cobalt–molybdenum–tellurium–phosphorus oxide catalyst has shown that it consists of a-$CoMoO_4$#, MoO_3, P_2O_5, TeO_2, and

†Here b-$CoMoO_4$ is a modification of cobalt molybdate characterised by an octahedral oxygen environment of the molybdenum.

#Here a-$CoMoO_4$ is a low-temperature modification of cobalt molybdate with four-coordinated molybdenum and six-coordinated cobalt.

a chemical compound (the x-phase§). The active component of the catalyst is molybdenum trioxide promoted with tellurium dioxide in the oxidation of propene to acrylaldehyde, but α-$CoMoO_4$ in the oxidation of acrylaldehyde to acrylic acid[35].

Several general ideas have now been formulated on the selective oxidation of alkenes and in particular of propene[36,37]. In selective oxidation activation of the propene molecule requires that the catalyst should possess certain acid–base properties in order to abstract α-hydrogen and form an allyl group. Furthermore, the catalyst should possess appropriate redox parameters in order to bind this group by electron transfer from an allyl π-orbital to a d-orbital of the cation and produce a definite charge on it, since the subsequent reaction depends on the sign of this charge.

A molecule of an oxygen-containing product is formed by nucleophilic addition of oxygen ions from the crystal lattice to the activated hydrocarbon complex. Thus oxygen ions implanted in the catalyst lattice are nucleophilic reagents devoid of oxidising properties, while lattice cations act as oxidant in selective oxidation, activating hydrocarbons and forming a hydrocarbon residue having electrophilic properties. However, what properties of a surface cation on the catalyst influence activation of the alkene remains an open question.

It has been suggested[38,39] that catalysts of partial oxidation are characterised by metal–oxygen double bonds. It has been shown for molybdates of various elements that on those containing Mo=O bonds oxidation takes place via an allyl group. Such bonds are not present in catalysts of complete oxidation, such as molybdates of Groups I and II elements having the scheelite structure. The direction of oxidation of an alkene is assumed[30] to be independent of the nature of the metal M and determined solely by the electronic structure of the bond: low polarity of the M=O bond favours selective oxidation; with a strongly polar bond electrophilic attack of π-electrons of the alkene is probable with rupture of the ethylenic bond.

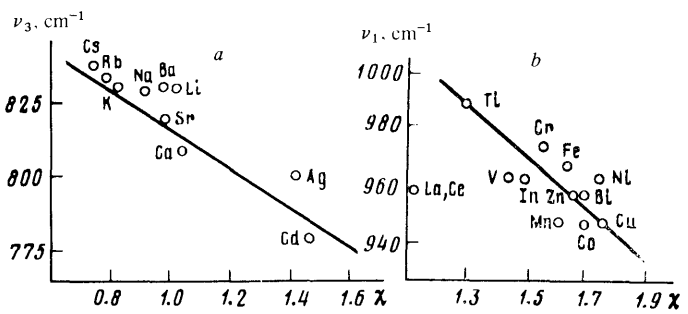


Figure 1. Comparison with the cation electronegativities χ of the wavenumbers ν of the characteristic bands in the infrared spectra of molybdates for the bonds: *a*) Mo=O, ν_3; *b*) Mo–O, ν_1.

The frequency of vibration of single and double-molybdenum–oxygen bonds depends on the nature of the cations present in molybdates[39]: the absorption bands move to lower frequencies with increase in electronegativity of the elements involved, which indicates increasing lability of these bonds (Fig.1), while the rate of allylic oxidation of propene increases (Fig.2). The formation of metal–oxygen double bonds may be promoted by oxygen vacancies appearing on the surface during the reaction, as is assumed in the mechanism of the oxidation of propene to acrylaldehyde on a uranium–antimony catalyst[40], and also by the introduction of additives, e.g. of tellurium into cadmium molybdate[41].

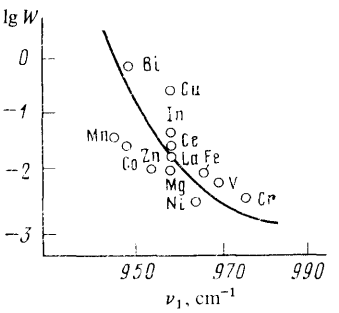


Figure 2. Specific rate of formation W of products of allylic oxidation on molybdates as function of wavenumbers of infrared absorption bands due to the Mo=O bond.

Several studies[42–50] have revealed the activating effect of excess of molybdenum trioxide on the catalytic properties of molybdates in various types of oxidation of alkenes. Such excess was assumed to be necessary to maintain the stoichiometric composition of the surface layer with loss of molybdenum during catalysis[46], to promote complete interaction of the initial salts during preparation of the normal molybdate[48], and also apparently to produce structural defects[42,43,49,50].

X-Ray diffraction, infrared spectroscopy, conductivity measurements, and density measurements on cobalt, iron, and chromium molybdates containing excess of molybdenum trioxide indicate that such excess within certain limits leads to formation of an imperfect structure, a solid solution. The defect structure produces a considerable increase in catalytic activity of the system towards the oxidation of propene[50–52] (Fig.3).

The probability of the dissolution of molybdenum trioxide in a molybdate is determined by the similarity of their structural fragments, comprising alternating oxygen octahedra and tetrahedra populated by the corresponding metal cations[53]. The degree of substitution of cations in the molybdate structure by the molybdenum ion is largely determined by the closeness of their ionic radii and also by the configuration of the electron shells. Absence of such correspondence, e.g. in indium and bismuth molybdates, leads to formation of a mechanical mixture of the molybdate with molybdenum trioxide[50].

It has been shown for isostructural cobalt and magnesium molybdates that introduction of excess of molybdenum trioxide not only increases substantially the rates of oxidation of propene to acrylaldehyde but also results in almost the same rates, evidence that active centres of closely similar composition have been formed[54].

A favourable influence of excess of one of the components on the activity and selectivity of a catalyst has been established also in other cases. Thus in the iron–antimony oxide system the selectivity of the chemical compound $FeSbO_4$

§Here the x-phase is a chemical compound formed in the tellurium–molybdenum oxide system at 425–450 °C.[35]

in allylic oxidation is considerably increased in the presence of excess of Sb_2O_4.[55] It was suggested that the latter suppresses the presence of free iron oxide, which is active in further oxidation[56,57]; formation of new chemical compounds—$FeSb_2O_4$ and $Fe_2Sb_2O_7$—may well be probable[58]. The high selectivity of the $FeSbO_4$–Sb_2O_4 system has been attributed[59] to interaction at the phase boundaries.

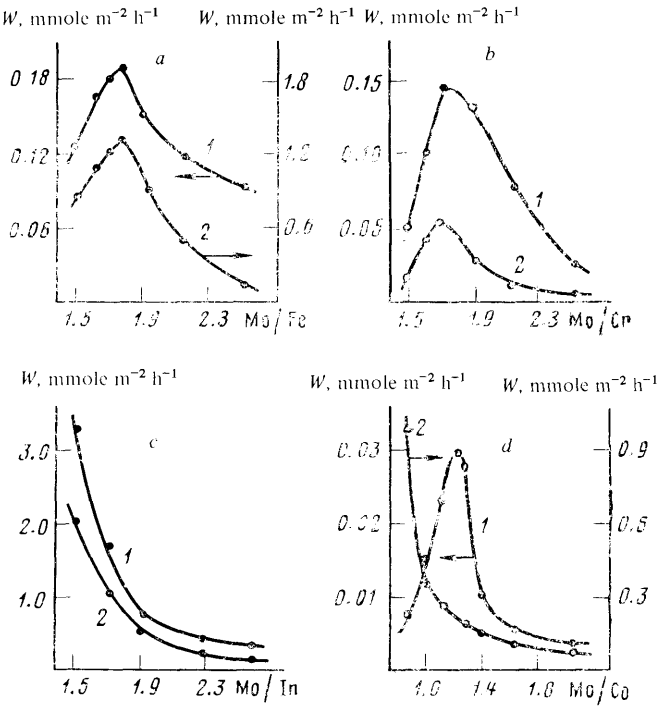


Figure 3. Variation[50] in specific rate of formation of *1*) acrylaldehyde; *2*) carbon dioxide with Mo/M ratio for M: *a*) Fe; *b*) Cr; *c*) In; *d*) Co.

Comparison of the activities of catalysts having antimony–iron ratios of 1 and 2 towards the oxidation of propene to acrylaldehyde in oxidising and reducing media indicates[55] that the decrease in the yield of carbon dioxide with simultaneous increased formation of acrylaldehyde is due to modification of the properties of oxygen on the catalyst surface: with excess of Sb_2O_4 on the surface of $FeSbO_4$ a thin (<20 Å) antimony-enriched layer is formed, responsible for the selective oxidation of propene to acrylaldehyde. Considerable enhancement of selectivity of oxidation to acrylaldehyde is possible[60] on an $FeSbO_4$ catalyst on which a small quantity (1–2 atomic layers) of Sb^{5+} ions have been deposited.

Excess of an oxide held in solid solution also enhances activity[61]. In the antimony–tin oxide system containing 5 mass % of antimony the latter is present in the SnO_2 lattice as Sb^{5+} ions, but at higher contents as a mixture of Sb^{5+} and Sb^{3+}. Calcination leads to separation of an oxide phase, identified as a two-dimensional layer of Sb_2O_4. A two-phase catalyst containing 18.7 mass % of antimony is the most selective with respect to acrylaldehyde. The effective catalyst comprises an oriented film of Sb_2O_4 deposited on an Sb^{5+}–SnO_2 solid solution[61].

The matching of activating components to simple and binary oxides with the aim of improving the effectiveness of catalysts has led to considerable complication of their composition. At the present time multicomponent systems are used in industrial production, and the majority of patents propose catalysts containing at least four different elements (Table 1). The phase composition of most mixed catalysts and the function served by their individual components have not yet been elucidated.

It is noteworthy that molybdenum predominates in almost all the catalysts listed in Table 1. Molybdenum trioxide is known as a relatively inactive but highly selective catalyst for the oxidation of propene to acrylaldehyde, and is usually employed in admixture with other oxides. Preparation of a mixed catalyst may involve various types of interaction of the trioxide with the other oxide components—formation of chemical compounds such as molybdates, solid solutions, and mechanical mixtures.

Table 1. Catalysts for the oxidation of propene to acrylaldehyde and acrylic acid.

Catalyst	Ref.
$K_{0.1}Ni_{2.5}Co_{4.5}Cr_3BiP_{0.5}Mo_{12}O_x$	[62]
$Cr_{0.5}K_{0.1}Ni_{2.5}Co_{4.5}Fe_3BiMo_{12}O_x$	[63]
$Mo_{12}Cu_{0.1-9}Te_{0.2-0.8}Sb_{0.2-15}O_{36.8-85.5}$	[64]
$W_{0.5}Cs_{0.2}Ni_{2.5}Co_{4.5}Cr_2BiMo_{12}O_x$	[65]
$K_{0.07}Mg_{4.5}Fe_4Bi_2P_{0.5}Mo_{12}O_{51}$	[66]
$Mo_{12}BiFe_{12}Co_1NiBe_2P_{0.5}KO_x$	[67]
$Mo_{12}V_{2-11}Cu_{1-6}Cr_{0-1}W_{0-12}O_x$	[68]
$Ce_3W_{1.2}V_3Mo_{12}O_x$	[69]
$Mo_{12}Cu_{0.05-3}B_{0.001-0.1}P_{0.1-5}Sb_{0.001-1}V_{0.5}K_{0.05-5}O_x$	[70]
$Mo_{8-18}V_{0.1-6}Cu_{0.1-6}Ge_{0.1-6}O_x$	[71]
$Mo_{12}P_2Cr_{0.5}Zr_{0.5}Sn_{0.5}K_2O_x$	[72]

The high activity and the selectivity of multicomponent oxide systems has been explained[54] on the assumption that most of the active centres are grouped at the boundaries between individual crystallites, where different kinds of ions differing in charge and coordination coexist, and where the diffusion of oxygen, the adsorption of reactants, and the transfer of charge are accomplished with the least consumption of energy. Examination of a catalyst of general composition $M_n^{2+}Mo_{12}Bi_{0.75}O_x$ revealed the phases $M^{2+}MoO_4$, $Bi_2(MoO_4)_3$, MoO_3, and also strongly disintegrated iron molybdate; some of the ferric ions can partly penetrate molybdenum oxide and bismuth molybdate, while some of the ferrous ions are dissolved in M^2MoO_4.[73]

Numerous examples have been published of the interpenetration of ions when molybdenum trioxide is deposited on an "inert" carrier[74–80]. Thus on silicon dioxide a limiting concentration exists (~8 mass %) above which polymolybdate particles are formed and then crystallites of molybdenum trioxide. Below this concentration the catalyst contains particles of molybdosilicic acid and dimolybdates, while Mo–O fragments appear implanted in the silica structure[74,75]. It has also been shown[76] that silicon ions incorporated into molybdenum trioxide stabilise the hexagonal structure of the latter.

Calcination of a molybdenum oxide catalyst deposited on alumina and containing <9 mass % of molybdenum results in dispersion of the molybdenum as a monolayer, but with higher contents some bulk phase is observed[77]. Ignition causes molybdenum atoms to migrate into the interior of the

γ-alumina. According to X-ray electronic spectroscopy this is accompanied by displacement of the 3*d* line in the molybdenum spectrum to higher bond energies, as a consequence of transition of molybdenum from a covalent state in surface oxy-anions to a more ionic state in cavities of the crystal lattice[78]. A low molybdenum content (1.5 mass %) is almost entirely located in tetrahedral cavities of the alumina lattice and cannot be reduced. Increase in the content is accompanied by increase in the proportion of surface molybdenum in octahedral coordination and enhancement of the reducibility of the catalyst[79].

Unlike ions deposited together interact with the substrate. In the cobalt(II)–molybdenum(VI) oxide system on alumina the molybdenum ions prevent penetration of cobalt ions into the lattice with formation of the spinel $CoAl_2O_4$ and facilitate reduction of cobalt to the metal. The appearance of metallic cobalt in turn initiates reduction of molybdenum by atomisation of hydrogen molecules and diffusion of hydrogen atoms towards the molybdenum ions, i.e. by a "spillover" effect. It is significant that surfaces differing in composition can be formed in different media: heat-treatment of the cobalt–molybdenum–aluminium oxide system in air tends to enrich its surface with molybdenum ions, but reduction of the catalyst enriches it with cobalt ions[73]. Migration of molybdenum ions takes place during heating. After γ-alumina has been impregnated successively with solutions of ammonium paramolybdate and cobalt nitrate, subsequent heating at 500 °C produces a redistribution of cobalt and molybdenum ions. As a result, a layer of molybdenum oxide is formed on the surface of the catalyst, and a layer of cobalt oxide directly covers the surface of the carrier[80].

It is now suggested that the catalytic activity and selectivity of several oxide systems based on molybdenum (the trioxide on silica and on alumina) are determined by stabilised salts of heteropoly-acids attached to the surface[81–84]. Molybdenum(VI), tungsten(VI), and vanadium(V) are known to form heteropoly-acids with heteroatoms—phosphorus, silicon, arsenic, etc.—that are strong many-electron oxidants and at the same time inorganic acids possessing high Brønsted acidity[85–87]. Heteropoly-acids are used as homogeneous catalysts for the partial oxidation of organic compounds[88], including alkenes[89]. In the Reviewer's opinion, however, further evidence is required to support the view that heteropoly-acids have a decisive role in the activity of oxide systems in heterogeneous catalysis.

Supported molybdenum catalysts containing definitely coordinated molybdenum ions have proved several times more active and more selective than corresponding catalysts prepared by impregnation[90]. The active centres are coordinatively unsaturated molybdenum ions combined with Brønsted acid centres of the carrier. Thus the construction of an active surface by attaching complexes of definite composition to a catalyst and the formation of clusters of several identical or different metal atoms may prove an effective method for enhancing the activity and the selectivity of a catalyst.

III. OXIDATION OF PROPENE TO ACETONE AND ACETIC ACID

The production of acetone and its analogues by the gas-phase catalytic oxidation of alkenes has many advantages over other methods (cheap starting materials, absence of corrosive agents, simple apparatus, etc.). Various catalysts have been proposed, including binary molybdenum-containing systems, for the single-stage oxidation of propene to acetone[91–95].

It had been shown earlier[91] that selective formation of acetone takes place on the Co_3O_4–MoO_3 system over the range of cobalt–molybdenum ratios 9–4 : 1.

This work was continued by investigating the oxidation of propene to acetone on various oxides containing 10% of molybdenum trioxide[92]. The most effective in this series was a tin–molybdenum oxide catalyst: acetone begins to be formed even at 110–120 °C, and at 170 °C the selectivity with respect to acetone is 80–85%.

The titanium–molybdenum oxide system is somewhat less effective than a tin–molybdenum oxide catalyst. It is catalytically active at 110 °C, but the rate of formation of acetone is lower than on the latter system. Isopropyl alcohol is formed on both systems at low temperatures.

The ion–molybdenum oxide system catalyses the formation of acetone above 150 °C, with a maximum rate at 200 °C (selectivity 80%). A chromium–molybdenum oxide catalyst is active above 200 °C, and approaches the cobalt–molybdenum oxide system in activity. Acetone is formed also on oxide systems of molybdenum with vanadium, nickel, copper, and zinc, but the selectivity is low.

Study of the aluminium–molybdenum oxide system[93–95] containing up to 30 mass % of molybdenum has established that water vapour increases considerably its catalytic activity and selectivity in the oxidation of propene to acetone. The active centres presumably represent a combination of reduced and oxidised forms of molybdenum(V) and (VI). Catalytic activity is determined in considerable measure by the acidity of the surface, which is governed by the presence of molybdenum(V) ions formed by reduction of the catalyst. Molybdenum(VI) ions are involved in oxidising intermediate products. The surface acidity in turn influences the mobility and the reactivity of hydroxy-groups[94].

The investigations suggested, for the oxidation of propene to acetone, the scheme

$$CH_3{-}CH{=}CH_2 \xrightarrow{+H^+} CH_3{-}{}^+CH{-}CH_3 \xrightarrow{+OH^-} \rightarrow [CH_3{-}CHOH{-}CH_3]_{ads} \xrightarrow{O} (CH_3)_2CO + H_2O \ .$$

The intermediate complex was assumed[94] to be an isopropoxy-group.

Kinetic study of the formation of acetone by the oxidation of propene on an iron–molybdenum oxide catalyst (Mo/Fe = 1.5) showed that the quantity of acetone formed varies linearly with the partial pressures of water vapour and propene, whereas the order with respect to oxygen is zero. The reaction velocity is given by the equation

$$V = k \cdot P_{H_2O} \cdot P_{C_3H_6} \ .$$

Either acetone or acrylaldehyde can be obtained depending on the temperature and also on the presence or absence of water in the reaction zone on iron molybdate. Hence an iron–molybdenum oxide catalyst can be regarded as bifunctional. Hydroxy-groups present on the surface in the presence of water vapour are assumed to take part in the hydration of propene, whereas oxygen ions attached to molybdenum effect the formation of acetone[96]. The mechanism of the oxidation of propene to acetone on an iron–molybdenum oxide catalyst has been assumed[97] to involve a stage of hydration of propene to isopropyl alcohol followed by oxidation of the secondary alcohol to acetone.

According to some workers[98] the oxidation of propene on a tin–molybdenum oxide system yields mainly acrylaldehyde and acrylic acid, but according to others[99,100] acetone and acetic acid. Information on the phase composition of this catalytic system is also contradictory: formation of a mechanical mixture of oxides, a chemical compound, or a solid solution based on tin dioxide have been suggested[99],

but evidence has been provided[101] for the formation of a solid solution based on molybdenum trioxide. It has been established that the phase composition and the direction of the partial oxidation of propene depend significantly on the method of preparation of the catalyst—the starting materials, the temperatures of coprecipitation and ignition, etc.

Pure tin dioxide is almost completely devoid of surface acid centres[102]. As molybdenum trioxide is added, the concentration of active centres increases significantly. This is to some extent supported by experiments undertaken by Buiten[103], in which the trioxide was deposited on the dioxide at high temperatures by means of water vapour, which interacts with the former to give the volatile species $MoO_2(OH)_2$, and this migrates through the gas phase to settle on the surface of the dioxide. The activity of the specimen in the oxidation of propene to acetone and acetic acid is thus greatly enhanced.

A parallelism has been established[104] between the activity of a tin–molybdenum oxide catalyst in the isomerisation of but-1-ene and the rate of oxidation of propene to acetone. The rate of isomerisation of an oxide catalyst depends on the surface acidity[105], so that active centres formed by the combination of tin dioxide and molybdenum trioxide are probably acidic in character. The acid–base properties of specimens are in turn determined by the method of preparation. Thus at high ignition temperatures irreversible desorption of hydroxy-groups—acid centres promoting the formation of acetone—may occur on the catalyst surface, with simultaneous increase in the relative number of metal ions, which are centres for the oxidation of propene to acrylaldehyde.

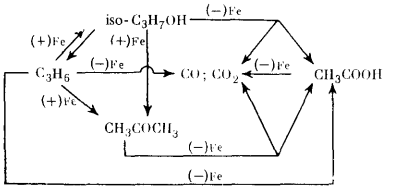
The effect of adding oxides of fourth-period transition metals to the tin–molybdenum oxide system has been investigated[106] on specimens of composition Mo : Sn : M = 3 : 1 : 0.15 (M = Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn). The catalysts were in all cases solid solutions based on molybdenum trioxide. The additives produced appreciable changes in activity and selectivity of the tin–molybdenum oxide catalyst. With the exception of cobalt and titanium they all enhanced the selectivity of formation of acetone, but the maximum yields achieved on the ternary catalysts varied: introduction of copper, zinc, manganese, and vanadium produced lower maximum yields of acetone than on the tin–molybdenum catalyst; chromium, nickel, and iron increased the maximum yield. Addition of 2 mass % of iron oxide was the most effective for the production of acetic acid (Table 2).

Table 2. Oxidation of propene on Sn–Mo and Sn–Mo–Fe oxide catalysts[106].

Catalyst	t, °C	Yields of reaction products, mass %			
		C_3H_7OH	$(CH_3)_2CO$	CH_3COOH	CO_2
Sn–Mo	175	0.1	8.2	1.9	3.7
Sn–Mo–Fe	175	3.1	11.3	0.5	0.3
Sn–Mo	200	0	9.3	5.3	9.0
Sn–Mo–Fe	200	2.1	18.5	2.0	1.9

Experimental results obtained on a tin–molybdenum oxide catalyst have shown[107] that propene is oxidised to acetone mainly via isopropyl alcohol, but acetic acid is formed both from acetone and from this alcohol.

A similar investigation has been made on a tin–molybdenum–iron oxide catalyst, with comparison of the rates of oxidation of conversion products of propene. Oxidation of isopropyl alcohol on a catalyst containing added iron ions gives a rather higher yield of acetone than on a tin–molybdenum oxide catalyst, whereas the yields of acetic acid and carbon dioxide are diminished by factors of 2 and 3.6. It is significant that the acidity of a tin–molybdenum oxide specimen is diminished by the introduction of iron. The results suggest the scheme



for the oxidation of propene on a tin–molybdenum–iron catalyst[107]. It shows the influence of positive and negative iron ions on the activity of a tin–molybdenum catalyst in various intermediate reactions in the oxidation of propene.

Table 3. Effect of potassium ions on specific rate of formation of oxidation products of propene on an Sn–Mo–Fe oxide catalyst[108].

Catalyst	t, °C	W, mmole m^{-2} h^{-1}			S*, %	K**, %
		CO_2	CH_3COCH_3	CH_3COOH		
Sn–Mo–Fe	190	0.03	0.12	0.03	83	17
Sn–Mo–Fe	230	0.15	0.15	0.08	62	29
Sn–Mo–Fe+K***	190	0.02	0.30	0.02	94	21
Sn–Mo–Fe+K	230	0.15	0.50	0.04	87	39

*S = selectivity of oxidation of propene to acetone.
**K = conversion of propene.
***Quantity of potassium introduced 0.7 mass %.

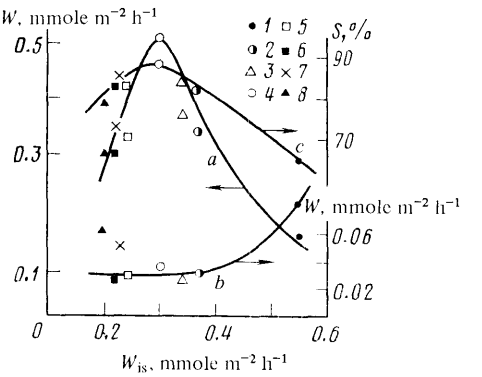


Figure 4. Variation[108] of: *a*) specific rate of formation of acetone; *b*) specific rate of formation of acetic acid; *c*) selectivity S of oxidation of propene to acetone with rate of isomerisation W_{is} of but-1-ene into but-2-ene on an Sn–Mo–Fe oxide catalyst containing added Group I elements: *1*) none; *2*) Li; *3*) Na; *4*) K; *5*) Rb; *6*) Cs; *7*) Cu; *8*) Ag.

The activity of a tin–molybdenum–iron catalyst and its selectivity of oxidation of propene to acetone are increased by the introduction of Group I elements[108]. The activity

depends on the quantity of additive, and reaches a maximum in the presence of 0.7 mass % of potassium. The yield of acetone is greatest at relatively high temperatures (Table 3).

Addition of alkali metals to a tin–molybdenum–iron oxide catalyst diminishes the surface acidity, the effect being greater the more basic the additive. Fig.4 shows the dependence of the specific rate of formation of oxidation products of propene on the acidity assessed from the rate of isomerisation W_{is} of but-1-ene into but-2-enes. With decrease in acidity the rate of formation of acetone passes through a maximum, and those of acetic acid and carbon dioxide decrease. The specific rate of formation of acetone increases more than the latter rate decreases, from which it may be concluded that the observed increase in activity is due mainly to the formation of new active centres.

The maximum specific rate of formation of acetone is achieved on catalysts containing added sodium and potassium ions[108]. The more basic the ions the higher the rate of formation of acetone and the lower the degradative oxidation of propene[108]. It can be concluded that high activity and selectivity of a catalyst in the oxidation of propene to acetone require an optimum acidity, which can be produced by introducing into a tin–molybdenum–iron oxide catalyst a definite quantity of alkali-metal ions depending on their basicity.

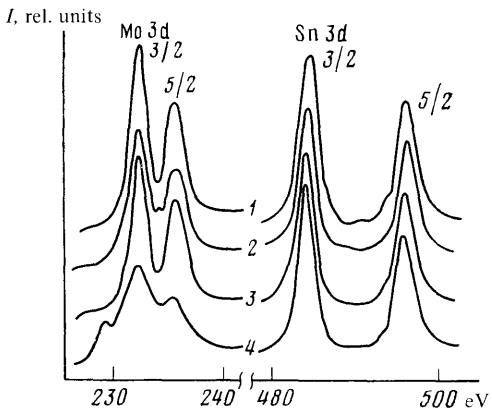
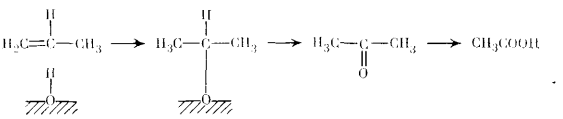


Figure 5. X-Ray electronic spectra of Sn–Mo–Fe oxide catalysts:
1) after roasting in oxygen at 250 °C;
2) after vacuum treatment at 425 °C;
3) catalyst with added potassium after roasting in oxygen at 250 °C;
4) catalyst with added potassium after vacuum treatment at 425 °C.

The incorporation of alkali metals into tin–molybdenum–iron oxide catalysts affects their X-ray electronic spectra[108]. Only tin, molybdenum, and oxygen ions are found on the surface, while iron and potassium ions are absent, which indicates that they have entered into the molybdenum trioxide structure. It is significant that reduction of a promoted catalyst affects mainly the oxidation state of the molybdenum ions, while tin ions remain almost unchanged (Fig.5). The spectrum of a reduced tin–molybdenum–iron oxide catalyst contains a weak signal due to Mo^{5+}, but in those of a promoted catalyst the signals due to reduced forms of molybdenum are considerably strengthened. The Mo^{5+}–O bond is less stable than Mo^{6+}–O, so that the introduction of potassium ions is responsible for the lability of the molybdenum–oxygen bond. The activating effect of alkali-metal ions in a tin–molybdenum–iron oxide catalyst apparently consists in changing the valency of the molybdenum, with the consequent appearance of new centres, on which alkenes undergo partial oxidation to ketones.

A mechanism of oxidation of propene to acetone on a tin–molybdenum oxide catalyst, involving formation of an alkoxy-group, was suggested by Buiten[103]. In the presence of deuterium oxide it proved difficult to exchange the hydrogen atom attached to the middle carbon atom in propene and also in isopropyl alcohol[109]. This was explained by interaction of propene with a surface hydroxyl to form an isopropyl group attached to a surface oxygen atom, and this group is an intermediate in the oxidation of propene to acetone and acetic acid:



Several results led Buiten[103] to deny intermediate formation of isopropyl alcohol in the oxidation of propene to acetone. Indeed, oxidation of the alcohol produces less acetone than expected, and furthermore the relative rates of formation of acetone and propene do not correspond to the rates of oxidation of propene to acetone and acetic acid according to the above scheme. Buiten's suggested mechanism involving detachment of the hydrogen atom from the middle carbon atom of the isopropyl group was supported by an investigation of the kinetic isotope effect of hydrogen involving comparison of the rates of oxidation of 2-deuteropropene $CH_2{:}CD.CH_3$ and non-deuterated propene[109].

Moro-Oka et al.[91,92] used a tracer method to determine the source of oxygen in the formation of acetone. In experiments on a tin–molybdenum oxide catalyst oxygen-18 was detected only in the acetone, whose content of the isotope was the same as that in the water present in the reaction system. Hence rapid exchange between adsorbed oxygen and the oxygen of the water does not take place, and oxygen-18 apparently passes into acetone by direct interaction between propene and adsorbed water[104]. Two mechanisms for the formation of acetone were suggested on the basis of these results:

$$CH_2{=}CH{-}CH_3 \xrightarrow{+OH^-} CH_2{-}CHOH{-}CH_3 \xrightarrow{\text{migration of H atom}}$$
$$\rightarrow {}^{+}CH_3{-}CHO{-}CH_3 \xrightarrow{-H^+} CH_3{-}CO{-}CH_3 \qquad (1)$$

$$CH_2{=}CH{-}CH_3 \xrightarrow{+H^+} CH_3{-}{}^{+}CH{-}CH_3 \xrightarrow{+OH^-}$$
$$\rightarrow CH_3{-}CHOH{-}CH_3 \xrightarrow{-2H^+} CH_3{-}CO{-}CH_3 + H_2O \qquad (2)$$

The first mechanism involves addition of a hydroxy-group to the π-bond of the alkene with formation of a σ-complex, which is converted into the carbonyl compound with liberation of a hydrogen atom. In the second mechanism addition of a proton produces a carbonium ion, subsequent attack on which by a hydroxy-group gives the secondary alcohol, which is oxidised to acetone. Since isopropyl alcohol was detected among the reaction products, the latter mechanism was regarded[104] as the more probable.

A scheme has been suggested for the oxidation of propene on a tin–molybdenum–iron catalyst[107,110] according to which acetone is formed below 150 °C mainly from isopropyl alcohol, but above 200 °C directly from propene.

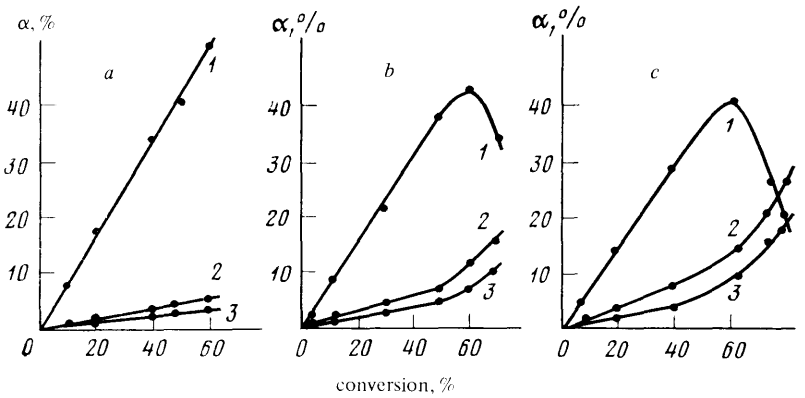


Figure 6. Degree of conversion α of propene into: *1*) acetone; *2*) carbon dioxide; *3*) acetic acid as function of total conversion[110] at various temperatures (°C): a) 190; *b*) 210; c) 230.

Formation of isopropyl alcohol was not observed[108] in the oxidation of propene on a promoted tin–molybdenum–iron catalyst at 170–210 °C. Comparison of the rates of accumulation of acetone in the oxidation of propene and of the alcohol showed that the latter is converted mainly into propene, only a small proportion being oxidised to acetone. This suggested that in the oxidation of propene the formation of acetone does not involve isopropyl alcohol:

$$CH_3{-}CH{=}CH_2 \xrightarrow{+H_2O_{ads}} [CH_3CHOHCH_3]_{ads} \xrightarrow{+O_{ads}}$$

$$\begin{array}{ccc} CH_3COCH_3{}_{ads} & & H_2O_{ads} \\ \downarrow\uparrow & & \downarrow\uparrow \\ CH_3COCH_3 & & H_2O \end{array}$$

Propene reacts with molecularly absorbed water to form a complex of alcoholate type, whose interaction with adsorbed oxygen releases a molecule of water with the formation of acetone. The zero order with respect to oxygen indicates that the latter is not involved in the rate-determining stage of acetone formation. In the absence of oxygen, however, acetone is not formed, and adsorbed oxygen is apparently involved in oxidation of the alcoholate complex.

Mechanisms of the formation of acetic acid in the oxidation of propene on catalysts containing molybdenum have been discussed[103,104,110]. It may be formed as a result of degradation of the activated complex of propene at the double bond[104] or by the oxidation of acetone[103]. Study of the oxidation of acetone in admixture with propene[108,110] has shown that at low temperatures acetone is hardly oxidised at all, acetic acid being formed from propene, whereas at high temperatures it is formed from propene and from acetone. Discrepancies in the literature concerning the mode of formation of acetic acid are apparently due to the temperature ranges over which this reaction has been studied.

Fig.6 illustrates the dependence of the yields of acetone, acetic acid, and carbon dioxide on the conversion of propene. At 190 °C they increase linearly with the conversion: i.e. acetic acid is formed by the degradative oxidation of propene at the double bond. At 210 and 230 °C the yield of acetone passes through a maximum, while those of acetic acid and carbon dioxide increase rapidly as a consequence of subsequent oxidation of acetone.

* * *

Thus in both molybdates and solid solutions based on molybdenum trioxide partial catalytic oxidation of propene takes place on active centres containing molybdenum, but the direction of oxidation and the oxidation state of the molybdenum cation are determined also by the nature of the functional groups present in the centres.

From the totality of results obtained on the physicochemical properties of molybdenum-containing oxide systems it can be concluded that the production of practically effective catalysts requires the presence of activating additives, which dissolve in the catalyst structure, promote the appearance of additional defects, and participate in the formation of an active surface.

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Catalytic Polarographic Currents of Oxidants

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The state of the theory and practice in an important field of polarography—the catalytic currents of oxidant-substrates—is examined. It has found extensive applications in the last ten years in the development of highly sensitive methods for the determination of a large number of substrates, catalysts, and polarographically inactive ligands. Attention has been given to the problem of the electrocatalytic reduction of molecular nitrogen for its fixation under mild conditions.
A systematic account is given of data for a series of inorganic and organic substrates and catalysts which transfer an electron to the substrate.
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I. INTRODUCTION

Catalytic currents in polarography, due to the regeneration of the depolariser via a chemical reaction, still attract much attention, mainly because they make it possible to increase appreciably the sensitivity of the analytical method and permit the determination of electrochemically inactive substances. However, the importance of catalytic currents goes beyond the analytical applications of polarography. In essence, these phenomena constitute the basis of the coulometric titration method and electrochemical synthetic processes with participation of electron transferring agents[1].

It is very likely that the fixation of atmospheric nitrogen, occurring in plant cells with participation of specific metal-containing enzymes[2,3], as well as many oxidation-reduction reactions constituting the basis of respiration, oxidative phosphorylation, and other processes important to life also occur under the conditions of the catalytic action of micro-elements. For this reason, examination of the available data on the mechanism of the occurrence of catalytic phenomena in polarography, to which this review is devoted, may be of general interest.

The review deals mainly with the reduction of a substrate by variable oxidation state metals; catalytic systems involving the oxidation of the substrate as well as catalysis by ligands (the complex is reduced or oxidised more readily than the aquo-ions) and the catalytic evolution of hydrogen are not discussed, because these two cases have been described quite adequately in other reviews[4,5] and monographs[6,7].

Catalytic currents of the type considered are manifested on polarograms as a rule by an increase of one of the diffusion waves of the catalyst metal and only in systems with hydrogen peroxide as the substrate does a separate reduction wave of the metal peroxide appear.

In the simplest case the mechanism of generation of the catalytic current can be represented schematically as follows:

$$\begin{array}{l} A + ne \rightarrow B \\ \uparrow\!\!_____| \\ B + S \xrightarrow{k} A \end{array} \quad , \qquad (1) \quad (2)$$

where A is the depolariser (the oxidised form of the catalyst), B the reduced form of the catalyst, and S the reagent (substrate or oxidant-substrate) participating in the chemical depolariser regeneration reaction. The catalytic current is determined by the rate of chemical reaction (2).

For a quantitative description of the catalytic currents arising via this scheme, an approximate solution was proposed initially[8,9] and then an exact solution[10], both based on the concept that the chemical depolariser regeneration reaction occurs in a thin layer of solution adjoining the electrode in the presence of an excess of the substrate.

When the reverse reaction (2) is neglected and when $k[S]_0\tau > 10$, the exact solution leads to the asymptotic equation

$$\bar{i}_c/\bar{i}_d = 0.81(k[S]_0\tau)^{1/2} , \qquad (3)$$

in which $\bar{i}_c$ is the average limiting catalytic current, $\bar{i}_d$ the average limiting diffusion current of the catalyst metal, k the rate constant for the forward reaction (2), $[S]_0$ the substrate concentration, and τ the drop period. The expression in square brackets in Eqn.(3) includes the stoichiometric coefficients, which depend on the nature of reaction (2).

A number of reviews have been devoted to the state of the theory and applications of catalytic polarographic currents[4,11-19], but examination of the literature shows that many important factors are still not clear. In particular, the causes of the differences between the rates of reduction of the substrate directly at the electrode and by reaction (2) have not been altogether elucidated. Andrieux et al.[20] considered the quantum-mechanical approach of Hush and Marcus to the relation between the rates of electronic transitions in the heterogeneous and homogeneous reactions. Attention has also been drawn[21] to the electrostatic factor, which increases the rate of interaction of the substrate and catalyst bearing different charges.

Studies have appeared in recent years in which the generation of the catalytic currents of the substrates is attributed to the formation of a complex BS and to electron transfer within the complex from the reduced form of the catalyst to the substrate. Such a mechanism has been proposed for both inorganic catalysts [W(VI)–ClO_3^- [22] and Mo(VI)–ClO_3^-–mandelic acid[23] systems] and for organic catalysts (dithiocarbamate–IO_3^-,[24] haemoglobin–H_2O_2, and iron(III) phthalocyaninetetrasulphonate–O_2 [25] systems), as well as for organic substrates in the Y(III)–L–dimethylformamide (DMF) system[26], which consist of carbonyl compounds: benzophenone, benzaldehyde, and crotonaldehyde.

The so-called coordination mechanism of the generation of catalytic currents has been proposed[16,17,27-30] and developed:

$$\begin{array}{l} A + n_1e \rightarrow B \ , \\ B + S \xrightarrow{k} BS \ , \\ \uparrow\!\!_____| \\ BS + n_2e \rightarrow B + P \ . \end{array} \qquad (4)$$

According to this mechanism the catalyst does not transfer electrons from the electrode to the substrate but merely activates the latter, increasing its reactivity in relation to reduction at the cathode. An equation has been derived for the description of the proposed mechanism[16,27-30]; despite the fundamental difference between the mechanisms, its form is close to that of Eqn.(3).

In order to account for the appreciable change in the catalytic current after the introduction of complex-forming substances into the solution, the formation of a ternary complex of the type BLS has been assumed in the last two concepts. One cannot rule out also another interpretation of this effect. Complex formation frequently accelerates electrochemical reaction (1) in both directions, so that irreversible reactions can actually become reversible. This should lead, in principle, to the acceleration of the homogeneous reaction (2) also.

Electron exchange within the complex is a reasonable alternative to the simple mechanism based on reactions (1) and (2), but we believe that the arguments adduced in its support in relation to the coordination mechanism are weak. Firstly, there is no direct evidence for the reduction of the substrate within the complex at the electrode. Secondly, the majority of substrates interact too weakly with the complex-forming metal to undergo an appreciable alteration in their reactivity. Nor is it clear why the interaction precisely with the reduced form of the catalyst are not with the initial, oxidised form is important for the generation of catalytic currents. Nevertheless, the coordination mechanism does not lack internal logic. Formally, systems with hydrogen peroxide behave seemingly in conformity with the coordination scheme: the metal peroxide compounds are reduced at the electrode.

An invariable condition for the appearance of the catalytic current of the substrate is its high electrochemical overvoltage. Many organic compounds do not exhibit a catalytic effect[21], because the electron transfer stage is in the vast majority of cases rapid (without overvoltage); on the other hand, the reason for the general irreversibility of the reduction of organic compounds is the occurrence of consecutive chemical reactions leading to the formation of covalent, inert C–H, C–C, etc. bonds. In such cases a significant increase of electron transfer to the substrate, with participation of the catalyst acting as an electron transferring agent, is impossible. The catalytic effect in polarography can be produced only by compounds in the electrochemical reduction of which the electron transfer stage is in fact slow. The reduction of the substrate can be accelerated by catalysts with a fairly high reduction potential and the necessary structure. The catalysts (among inorganic substances, these are usually transition metals) exist in aqueous solution in the form of monomeric or polymeric forms with different degrees of hydrolysis, depending on the conditions[31-35]. The activity of the catalyst depends on its state[36-39].

The wide variety of forms of the catalysts and the relatively few substrates make it possible to arrange the available literature data in terms of the nature of the oxidant-substrate.

II. CATALYTIC CURRENTS OF OXIDANTS

1. Catalytic Currents of Hydrogen Peroxide

The catalytic currents of H_2O_2 for the first row of transition metals are represented by the following systems: Ti(IV)–H_2O_2 and Ti(IV)–H_2O_2–L, where L = EDTA, nitrilo- triacetate (NTA), sulphosalicylate (SAL), and 4-(2-pyridylazo)-resorcinol (PAR);[40,41] V(V)–H_2O_2–H_2SO_4,[42] Fe(III)– H_2O_2–H_2SO_4,[43-52] and Fe(III)–H_2O_2–L, where L = bis-salicylidene-ethylenediamine and triethanolamine[53]; Cu(II)–H_2O_2–L, where L = Cl^- and α,α'-bipyridyl[54,55]. The second row of transition metals is represented by the first three numbers: Zr(IV)–H_2O_2,[56] Nb(V)–H_2O_2,[57] Nb(V)–H_2O_2–$H_2C_2O_4$,[58] and Mo(VI)–H_2O_2–L, where L = H_2SO_4 or acetate, phosphate, and hydrogen phthalate buffer mixtures[42,59,60]. The third row of transition metals is represented by the systems Hf(IV)–H_2O_2,[61] Ta(V)–H_2O_2–$H_2C_2O_4$,[62,63] and W(VI)–H_2O_2–L, where L = H_2SO_4, $H_2C_2O_4$, H_3PO_4, and H_3AsO_4,[42,64] and the Os(VIII)–H_2O_2 system[65]. The H_2O_2 catalytic reduction wave has also been observed for La(III).[66]

When the above transition metals are introduced into an aqueous solution of hydrogen peroxide, a catalytic wave appears on the polarogram whose height greatly exceeds the diffusion current of the metal and which is located at more negative potentials than the non-catalytic reduction wave of hydrogen peroxide and the transition metal. Os(VIII), for which the H_2O_2 catalytic wave coincides with its first two-electron reduction wave, is an exception[65]. The H_2O_2 catalytic wave has the form of a sharp or smooth peak, which is not due to adsorption effects, since the introduction of surfactants into the system does not cause the disappearance of the maximum in the polarographic wave[42,61]. The catalytic wave has the normal form without a maximum only for the Fe–H_2O_2 system[45-50]. Therefore the assignment of the M–H_2O_2 systems[67] to the group with a normal form of the limiting catalytic current plateau is incorrect.

A test of Koutecky's theory[10] in relation to the catalytic currents of the Fe(III)–H_2O_2 system demonstrated its validity[46]. The catalytic process in this system is described by the Haber–Weiss scheme[68] in which the rate-limiting stage involves the oxidation of Fe(II) to Fe(III) by hydrogen peroxide with formation of OH· radicals, which also oxidise Fe(II). Subsequently, this mechanism was confirmed also in relation to sulphuric and nitric acid solutions[69]. The presence of OH· radicals in the system was demonstrated by numerous instances of the decrease of the catalytic current in the presence of various organic substances[45,52] and monomers[70-72] which react with OH·.

In order to explain the catalytic H_2O_2 reduction currents in sulphuric acid solutions of the Fe(III)–H_2O_2–L system, investigators[48-50,53] proposed a coordination mechanism of their generation consisting in the fact that the iron(II) obtained at the electrode forms with H_2O_2 or HO_2^- the intermediate complex $[Fe(H_2O)_5(HO_2^-)]^+$, which is rapidly converted into $[Fe(H_2O)_5O]^{2+}$ and the latter is reduced at the electrode with regeneration of the Fe(II) aquo-ion. The slow stage of the process is the formation of the intermediate complex $[Fe(H_2O)_5O]^{2+}$, which is identical with the ferryl ion FeO^{2+}; this complex has properties analogous to those of the OH· radical. As already mentioned, the authors do not present direct evidence for the reduction of the oxygen atom (hydrogen peroxide) in $[Fe(H_2O)_5O]^{2+}$.

Titanium(IV) catalyses the reduction of H_2O_2 but at higher pH values than many other multicharged ions, even when a graphite rotating electrode is used[40]. The catalytic current in the Ti(IV)–H_2O_2 system is described by Koutecky's theory and is limited by the formation of $TiO(H_2O_2)^{2+}$ and the two-electron reduction at the electrode at pH 2–4 of the complex $[TiO(HO_2)]^+$, whose yield increases with pH as a consequence of the increase of the degree of acid dissociation of $TiO(H_2O_2)^{2+}$. The current i_c depends on the nature of the ligand: the presence of EDTA, SAL, and NTA increases i_c, while the addition of PAR decreases it.

The activating effect of ligands is due to the formation of Ti(IV) complexes, which react with hydrogen peroxide faster than the TiO^{2+} aquo-ions[40]. The catalytic activities of ligands increase in the sequence SAL < NTA < EDTA, which can be accounted for by the increasing stability of the complexes formed. Other metals of the titanium subgroup (zirconium[56] and hafnium[61]) catalyse the reduction of H_2O_2; the ease of reduction increases in the sequence Ti < Hf < Zr. As for titanium[40], the catalytic current is limited by the rate of formation of the intermediate complex between zirconyl[56] or hafnyl[61] and hydrogen peroxide. The current i_c in Zr(IV) and Hf(IV) solutions has a maximum (at pH 2.0 and 2.6) under the conditions of the maximum yield of the most active zirconyl or hafnyl ions[73].

Vanadium subgroup metals (vanadium, niobium, and tantalum) are readily hydrolysed[34] and tend to form many peroxide complexes[74] with different catalytic activities. The catalytic currents of the above elements are limited by the rate of formation of the peroxide compound. The vandium(V) peroxide compounds contain between one and four $H_2O_2(O_2^{2-})$ molecules[75]. The catalytic waves of vanadium, niobium, and tantalum have the form of a peak and are observed at less negative potentials than the waves due to metals and the non-catalytic reduction of H_2O_2; $E_{1/2}$ depends on the pH. As was to be expected, there is a complex dependence of i_c on the pH; the catalytic current has a maximum at the following pH:

Element	V(V)	Nb(V)	Ta(V)
pH	5.0	5.2	6.2

This behaviour of i_c for V(V) has been attributed[42] to the presence of its polymeric forms, which manifest different activities, and for Nb(V) and Ta(V) by the change in the composition of their peroxide compounds[56]. Since the vanadium(V) concentration in the above study[42] was very low (8×10^{-8} M), the maximum on the i_c–pH curve is most probably due to the presence in solution of various hydrolysed monomeric forms of vanadium(V) and not polymeric forms. In the presence of oxalic acid, the Nb(V) [58] and Ta(V) [62,63] electrode processes are limited by the formation of the peroxide compound $HMO_3.C_2O_4$, which is reduced to $HMO_2.C_2O_4$ (where M = Nb or Ca) with participation of two electrons.

The Cr(III)/Cr(II), Mo(VI)/Mo(V), Mo(V)/Mo(III), W(VI)/W(V), and U(IV)/U(III) systems, which possess reducing properties, are of greatest interest for the investigation of the catalytic currents of substrates in the presence of chromium subgroup elements (Cr, Mo, W and U). The H_2O_2 catalytic currents are known only for the Mo(VI)–H_2O [45,59] and W(VI)–H_2O_2 [45] systems. The formation of monomeric and polymeric forms of Mo(VI) [31,33,76,77] and W(VI) [31,33,78] in solution as well as a number of peroxides[76, 78,79] and complex compounds having different compositions are responsible for the complex form of the dependence of i_c on the pH and the catalyst concentration. The presence of a maximum on the i_c–pH curve[45], the dependence of its position and intensity on the nature of the buffer solution[45], the presence of a maximum on the i_c–c_{buff} curve for the phosphate buffer solution at pH 4.0,[59] and the decrease of i_c on passing from $HClO_4$ to H_3PO_4 solutions[45] have been explained on the basis of these ideas. The decrease of i_c in the phosphate buffer solution at pH 4.9 [45] on passing from vanadium to tungsten has likewise been accounted for from this standpoint.

The rate-limiting stage is the formation of the peroxide compound, which is reduced with participation of two electrons. The attempt[45] to explain the dependence of i_c on the pH by the presence of different polymeric forms reacting with H_2O_2 at different rates is in our view incorrect, since the Mo(VI) concentration was so low (3.2×10^{-6} M) that Mo(VI) was present only in the monomeric form[33,76]. The dependence of i_c on the pH is therefore associated with the presence of its different hydrolysed forms interacting with H_2O_2 at different rates.

In the manganese subgroup (Mn, Te, and Re) a catalytic H_2O_2 polarographic reduction wave is observed only for Te.[80] It is believed that in the homogeneous catalytic reaction the H_2O_2 oxidises the Te(V) formed to Te(VII).

The metals of the platinum subgroup (Ru, Rh, Pd, Os, Ir, and Pt) are characterised by a high oxidation potential and and extremely high capacity for hydrolysis and complex formation[31,79,81–84], which complicates the observation of the H_2O_2 catalytic currents. Ruthenium(VIII) is a stronger oxidant than osmium(VIII),[85] so that, in contrast to OsO_4, RuO_4 cannot give rise to H_2O_2 catalytic waves. The aquo- and hydroxo-complexes of certain platinum subgroup metals, for example Rh(III) and Ru(IV) (Ginzburg et al.[84] p.99) are extremely inert in processes involving the substitution of water molecules in the inner sphere of the ion by other ligands, which is probably the reason for the small number of examples of catalytic currents in platinum metal–oxidant systems; only two such examples are known: Os(VIII)–H_2O_2 [65,86] and Ru(III)–NH_2OH.[87]

The H_2O_2 catalytic wave in osmium(VIII) solutions[65,86] is observed in the positive range of potentials; with increase of $c_{H_2O_2}$, the current i_c passes through a maximum. The electrode process is determined by the rate of oxidation of Os(VI) to Os(VIII).[65] In unbuffered solutions this process may be limited by the formation of the peroxide compound $OsO_4.H_2O_2$.[86]

The metals of the copper subgroup (Cu, Ag, and Au) exhibit a considerable tendency towards complex formation. Ag(II), Ag(III), and Au(III) compounds show no catalytic activity with respect to the electrochemical reduction of H_2O_2, which can be explained by their high oxidising capacity. The high rate of exchange of water molecules in the first coordination sphere ($k = 8 \times 10^9$ s^{-1}) of copper(II) aquo-complexes (Basolo and Pearson[35], p.138) favours the generation of the catalytic currents of the substrate. The catalytic wave in the Cu(II)–H_2O_2 system[54] at pH < 7 is located in the range of potentials of the first one-electron copper(II) reduction wave and is described by the Koutecky equation[10]. The rate-limiting stage is the oxidation of Cu(I) by hydrogen peroxide with formation of the initial depolariser and the OH· radical, the latter being consumed in the oxidation of Cu(I) and Cl^-.

In neutral unbuffered chloride media the catalytic wave incorporates both Cu(II) reduction waves[54], which is probably associated with a change in the composition of the layer near the electrode as a consequence of the oxidation of Cu(I). The possibility of the oxidation of the metallic copper formed under these conditions cannot be ruled out either.

In an acetate medium[55] the catalytic wave, having the form of a maximum, arises at potentials more positive (by 0.1 V) than the copper reduction wave (pH 4.6), while in the presence of α,α′-bipyridyl the catalytic wave coincides with the copper reduction wave. A coordination mechanism has been proposed (but not justified experimentally) for the catalytic currents in the systems investigated[55].

The catalytic H_2O_2 reduction current is observed in solutions of copper salts also in anodic processes. It has been found[87] that, at the potential of the anodic peak associated with the dissolution of the copper amalgam (at $E = -0.18$ V), a cathodic current maximum is observed in the presence of H_2O_2 or O_2, which is due to the fact that the catalytic H_2O_2 reduction current is much greater (by a factor of 10–15) than the anodic copper dissolution current. The catalytic reduction current is due to the oxidation of the Cu(I) formed

to Cu(II), which is reduced to Cu(I) at the amalgam dissolution potential. An analogous behaviour has been observed also for lead[87–89], the only representative of non-transition elements catalysing the reduction of H_2O_2. The electrode process generating the catalytic current includes the reaction where the pH(II) at the electrode is oxidised by hydrogen peroxide to Pb(IV), which is reduced electrochemically to Pb(II).[87] The catalytic H_2O_2 current is also observed in the reduction of oxygen at platinum[90] and gold[91] microelectrodes. The exaltation of the limiting current can be explained by the generation of oxygen as a result of the oxidation of the superoxide ion by hydrogen peroxide.

Thus the appearance of i_c in many systems is due to the formation of peroxo compounds (of Ti, V, Mo, W, Nb, Hf, Zr, and Ta) which are reduced at less negative potentials than the metal in the highest oxidation state. The rate-limiting stage is the formation of the peroxo-compound (complex). In many systems incorporating Cu and Pb hydrogen peroxide is reduced by the ion of the catalyst metal.

The catalytic H_2O_2 currents make it possible to detect very low concentrations of catalysts (from 1×10^{-5} to 1×10^{-9} M) and have found extensive applications in the determination of vanadium[42], iron[45,47,50], copper[55,87], zirconium[56], niobium[57,58], molybdenum in soils[59] and granits[60], hafnium[61], tantalum[57,62], tungsten[42], osmium[65,86], and technetium[79]. Molybdenum[92] and titanium[41] (using a graphite electrode), copper[87], lead[87, 89] (in combination with amalgam polarography), and oxygen (using a rotating platinum[90] or gold[91] microelectrode) can be determined with a high sensitivity (to within 1×10^{-6} M). The catalytic H_2O_2 currents have been used successfully also for the investigation of the complex formation reaction between tantalum and oxalic acid[62] and between tungsten(VI) and oxalic, phosphoric, and arsenic acids[64].

2. Catalytic Currents of Hydroxylamine

The oxidising properties of hydroxylamine[93,94] have also been used to obtain its catalytic reduction currents. The first row of transition elements is represented by the systems Ti(IV)–NH_2OH–$H_2C_2O_4$,[95] Ti(IV)–NX_2OH (where X = H or D),[96,97] V(V)–NH_2OH,[98] Fe(III)–NH_2OH–$N(CH_2CH_2OH)_3$,[99] Ni(II)–NH_2OH–CN,[100] and Ni(II)–$NH_2(CH_2)_2NH_2$–CN,[100] the second row is represented by the system Nb(V)–NH_2OH [101, 102] and Ru(III)–NH_2OH,[103] while among the third row elements there are literature data only for tungsten: W(VI)–NH_2OH [104] and W(VI)–NH_2OH–L, where L = ascorbic acid, salicylic acid, catechol[105–107], etc. In the case of titanium-containing systems the catalytic current is limited by the rate of oxidation of titanium(III) ions by hydroxylamine with formation of titanium(IV) and the $NH_2^{\cdot}$ radical and is described by Koutecky's theory[10]. This is proved by the agreement between the rate constants for the oxidation reaction obtained by chemical and polarographic methods. The oxidation rate constants have the following values: 42.0,[95] 41.3,[96] 42,[108] 32.0,[109] and 43.4 litre mol^{-1} s^{-1}.[110] The mechanism adopted is also supported by data for the synthesis of α-aminosuccinic acid from maleic acid under the conditions of electrochemical generation of $NH_2^{\cdot}$ radicals[111].

The catalytic reduction of hydroxylamine in the presence of vanadium(V) in solutions at pH 1–5 is represented by a wave at a potential ~0.3 V more negative than $E_{1/2}$ for the V(V) → V(IV) waves[98]. According to the authors[98], the slow stage of the process is the formation of a complex between polymeric vanadium(V) and NH_3^+OH; the complex $V(V)_n$.NH_2^+OH is then reduced to $V(V)_n$ and $NH_2^{\cdot}$. It is difficult to agree with this, since the concentration at the electrode of the V(V) not bound in the complex at the potentials of the catalytic wave is zero and the mechanism involving vanadium(V) is therefore altogether impossible. We believe that the regeneration of the depolariser is due to the oxidation by hydroxylamine of the V(IV) formed. The introduction of EDTA and *trans*-1,2-cyclohexylenediaminetetra-acetate into the solution reduces i_c as a consequence of the formation of catalytically inactive complexes.

In the presence of the second representative of the vanadium subgroup, namely niobium, the catalytic hydroxylamine waves are observed in hydrochloric acid solutions with high HCl concentrations[101,102], where the catalyst exists predominantly in the monomeric form, which exhibits a higher catalytic activity than the polymeric and colloidal species. The authors[101] explained the generation of the catalytic current in terms of a coordination mechanism in which the rate-limiting stage is the formation of the intermediate complex Nb(IV).NH_3^+OH, which is reduced to Nb(IV) and NH_4^+; proof that the complex Nb(IV).NH_3^+OH is reduced is not presented.

The catalytic hydroxylamine current in the Fe(III)–NH_2OH–$N(CH_3CH_2OH)$ system at the Fe(II) oxidation potential (–1.05 V relative to the saturated calomel electrode) has been studied in 0.01–4.0 M NaOH.[99] The rate-limiting stage is the oxidation-reduction reaction of Fe(II) with NH_2OH. The validity of the mechanism adopted is demonstrated by the agreement between the rate constants for the reaction obtained by the chemical and polarographic methods. At 25 °C in 1 M NaOH they are respectively 205 ± 25 [97] and 198 ± 8 litre mol^{-1} s^{-1}.[99]

The catalytic hydroxylamine current in the Ni–CN–NH_2OH system[100] in neutral and alkaline media can be accounted for by the involvement of Ni(I) and Ni(0). The current i_c is a maximum at pH 8.5–9.5. Under these conditions, the system contains an appreciable amount of the hydrolysed form $NiOH^+$ (pK_1 = 9–9.5).[33] We therefore believe that one cannot rule out the involvement of the above form also in the reactions determining the catalytic current. When hydroxylamine is replaced by ethylenediamine, a catalytic current is also observed, but is smaller[100]. Thus the complexes incorporating elements with the d^8 configuration, which are fairly inert in the ligand exchange reaction in conformity with the crystal field theory[35], exhibit a fairly high reactivity after the introduction of one or even two electrons. Among the elements of the platinum group, the catalytic hydroxylamine current is observed only in the presence of ruthenium(III) [103] and is due to the oxidation by hydroxylamine of the Ru(II) formed and is described by the Koutecky theory; the rate constant for the rate-limiting stage in this process is 3×10^3 litre mol^{-1} s^{-1}. Since the ruthenium(II) aquo-complexes are inert (Cotton and Wilkinson[31], p.42), their observed reactivity is probably associated with the formation of a mixed complex.

A distinctive feature of tungsten, the only representative of the third row of transition elements, is the presence on the polarograms of the test systems of two catalytic hydroxylamine waves and of the catalytic wave of hydrogen ions[104–107]; the authors explained the appearance of the catalytic hydroxylamine waves in terms of a coordination mechanism. The rate-limiting stage for the first catalytic wave is the conversion of the intermediate tungsten(V) complex H_2WO_4.NH_2OH into the activated complex H_2WO_4.NH_3O^-, while for the second catalytic wave the rate-limiting stage involves the conversion of the intermediate tungsten(III) complex HWO.L.NH_3OH^- into the activated complex HWOL.NH_3O.[105,106] The charge of the species involved in the rate-limiting stage was determined using the dependence of the rate of reaction (the current i_c) on the ionic strengths[112]. The authors[105,106] do not present direct evidence for the reduction of the above species. One cannot rule out the possibility that the observed complex pattern may be associated with the presence of polymeric

forms of tungsten in solution, since at the concentrations investigated (5×10^{-4} M) a considerable proportion of the tungsten exists in the polymeric form[78]. This is indicated indirectly also by the decrease of the number of catalytic waves with decrease of the W(VI) concentration[105,106].

The rate constants for oxidation reactions with participation of substrates calculated from their catalytic polarographic currents in the presence of various catalysts and ligands at 20–25 °C.

Catalytic system	Reaction conditions	k_{tot}, litre mol^{-1} s^{-1}	References
Fe(III)—H_2SO_4—H_2O_2	0.5 *M* H_2SO_4	77.8	[46]
Fe(II)—H_2SO_4—H_2O_2*	0.5 *M* H_2SO_4	60	[45, 46]
Fe(III)—H_2SO_4—H_2O_2	0.0165 *M* H_2SO_4	69	[49]
Fe(III)—H_2SO_4—H_2O_2	0.26 *M* H_2SO_4	54	[49]
Fe(II)—H_2SO_4—H_2O_2*	0.005—2 *M* H_2SO_4	59.0±5.5	[69]
Fe(III)-complexone (IV)-H_2O_2	pH 2—5	10^3	[53]
Fe(III)—H_3Citr — H_2O_2	pH 9	10^3	[53]
Fe(III)—$NH_4C_2O_4$ — H_2O_2	pH 5	10^3	[53]
Fe(III)-PG-H_2O_2	pH 7.6	10^3	[53]
Fe(III)-CA-H_2O_2	pH 9	10^4	[53]
Fe(III)-AA-H_2O_2	pH 9	10^3	[53]
Fe(III)-SAL-H_2O_2	pH 10.7	$(48.00 \pm 1.55) \cdot 10^2$	[10]
Fe(III)-EDTA-H_2O_2	pH 2—5	10^4	[70]
Fe(III)-haemin-H_2O_2	pH 8—12	10^8—10^9	[44]
Fe(III)-catalase-H_2O_2	pH 1—7	10^7	[44]
Fe(III)-BSED-H_2O_2	pH 10	10^7	[44]
Fe(III)-BSED-H_2O_2	pH 6—11	10^6—10^8	[53]
Fe(III)-TEA-H_2O_2	pH 14	10^6	[44]
Fe(III)-TEA-H_2O_2	pH 7—12	10^5—10^6	[53]
Ti(IV)—H_2O—H_2O_2	pH 3.6	53	[40]
Ti(IV)-EDTA-H_2O_2	pH 3.6	$(6 \pm 2) \cdot 10^3$	[40]
Ti(IV)-NTA-H_2O_2	pH 3.6	$(2 \pm 1) \cdot 10^3$	[40]
Ti(IV)-SAL-H_2O_2	pH 3.6	$(3 \pm 2) \cdot 10^2$	[40]
Cu(II)—HCl—H_2O_2	0.1—1 *M* HCl	49	[54]
Cu(I)—HCl—H_2O_2*	0.1—1 *M* HCl	58	[54]
Cu(II)-bipy-H_2O_2	pH 4.6	$4.6 \cdot 10^4$	[55]
Ti(IV)-$H_2C_2O_4$-HA	0.2 *M* $H_2C_2O_4$	42	[95]
Ti(IV)-H_2O-HA	0.1 *M* H_2SO_4	41.3±1.5	[96]
Fe(III)-TEA-HA	1 *N* NaOH	205±25	[97]
Fe(III)-TEA-HA	0.1 *N* NaOH	595	[99]
Fe(III)-TEA-HA	1 *N* NaOH	198±8	[99]
Nb(V)-HCl-HA	4 *M* HCl	1	[101]
Nb(V)-HCl-HA	8 *M* HCl	45	[101]
Nb(V)-HCl-HA	11 *M* HCl	100	[101]
Ru(III)-Britton-Robinson buffer-HA	pH 6.7	$3 \cdot 10^3$	[103]
W(VI)-AA (first wave)-HA	pH 2.0	$4.25 \cdot 10^2$	[105]
W(VI)-AA (second wave)-HA	pH 2.0	$9.3 \cdot 10^3$	[105]
W(VI)-SA-HA (first wave)	pH 2.0	$2.1 \cdot 10^2$	[105]
W(VI)-CA-HA (first wave)	pH 2.0	$4.6 \cdot 10^2$	[106]
W(VI)-CA (second wave)-HA	pH 2.0	$1 \cdot 10^4$	[106]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.4 *M* H_2SO_4 + +0.25 *M* Na_2SO_4	$5.5 \cdot 10^4$	[114]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$5.3 \cdot 10^4$	[115]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.4 *M* H_2SO_4	$4.6 \cdot 10^4$	[116]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* $H_2C_2O_4$	$2.31 \cdot 10^4$	[117]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$5.11 \cdot 10^4$	[118]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$4.35 \cdot 10^4$	[118]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$4.48 \cdot 10^4$	[119]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* H_2SO_4	$4.31 \cdot 10^3$	[120]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.4 *M* H_2SO_4	$2.68 \cdot 10^4$	[122]
Ti(IV)—$H_2C_2O_4$—$KClO_3$**	0.2 *M* $H_2C_2O_4$	$2.2 \cdot 10^4$	[122]
Ti(IV)—$KClO_3$**	0.2 *M* $HClO_4$	$1.1 \cdot 10^5$	[126]
Ti(IV)—NaSCN—$KClO_3$**	0.2 *M* $HClO_4$	$2.2 \cdot 10^9$	[126]
Ti(IV)—$KClO_3$	0.1 *M* $HClO_4$	$6 \cdot 10^4$	[130, 132]
Ti(IV)-H_3 Trihydrox-$KClO_3$	0.1 *M* $HClO_4$	$6.9 \cdot 10^4$	[130, 132]
Ti(IV)—H_3 Citr—$KClO_3$	0.1 *M* $HClO_4$	$1.4 \cdot 10^4$	[130, 132]
Ti(IV)—H_2 Malic—$KClO_3$	0.1 *M* $HClO_4$	$1.3 \cdot 10^4$	[130, 132]
Ti(IV)—Tartr—$KClO_3$	0.1 *M* $HClO_4$	$1.4 \cdot 10^4$	[130, 132]
Ti(IV)—H_2 Malonic—$KClO_3$	0.1 *M* $HClO_4$	$0.57 \cdot 10^4$	[130, 132]
Ti(IV)—$H_2C_2O_4$—$KClO_3$	0.1 *M* $HClO_4$	$2 \cdot 10^4$	[130, 132]
Ti(IV)-CA-$KClO_3$	0.1 *M* $HClO_4$	$5.2 \cdot 10^4$	[132]
Ti(IV)—H Mandelic—$KClO_3$	0.1 *M* $HClO_4$	$11 \cdot 10^4$	[132]
Ti(IV)-HDPPA-$KClO_3$**	pH 1.6	$(1.5 \pm 0.3) \cdot 10^4$	[135]
Ti(IV)-EDTA-$KBrO_3$	pH 3.3	$6.7 \cdot 10^4$	[133]
Ti(IV)-HDPPA-$KBrO_3$**	pH 2.6	$(1.6 \pm 0.3) \cdot 10^4$	[135]
Mo(VI)—$KClO_3$	0.05 *M* H_2SO_4	$1.5 \cdot 10^3$	[139]
Mo(VI)—$KClO_3$	1 *M* H_2SO_4	$1.3 \cdot 10^3$	[139]
Mo(VI)—H_3 Citr—$KClO_3$	pH 1.1	$1.25 \cdot 10^3$	[144]
Mo(VI)—$H_2C_2O_4$—$KClO_3$	0.5 *M* H_2SO_4	$(7.2 \pm 0.8) \cdot 10^4$	[145]
Mo(VI)-H_3 Glucar-$KClO_3$	pH 1.1	$7.6 \cdot 10^6$	[147]
Mo(VI)—HGl—$KClO_3$	pH 1.7	$1.5 \cdot 10^5$	[148]
Mo(VI)-CA-$KClO_3$	pH 1.7	$8.9 \cdot 10^6$	[149]
Mo(VI)—H_2 Tartron—$KClO_3$	pH 1.7	$(2.0 \pm 0.5) \cdot 10^6$	[153]
Mo(VI)—H_2 Malic—$KClO_3$	pH 1.7	$1.3 \cdot 10^5$	[130]
Mo(VI)—H_2 Tartr—$KClO_3$	pH 1.7	$8 \cdot 10^5$	[130]
Mo(VI)—$KClO_3$—H_2— hydr.	pH 1.7	$7 \cdot 10^6$	[130]
Mo(VI)—$KClO_3$—H Mandelic	pH 1.7	$2.2 \cdot 10^8$	[130]
Mo(VI)—$NaClO_4$	1 *M* H_2SO_4	30	[138]
Mo(VI)—$NaClO_4$	0.05 *M* H_2SO_4	34	[139]
Se(IV)—BrO_3^-***	pH 3.6	$(4.6 \pm 2.9) \cdot 10^5$	[168]
W(VI)—ClO_4^-	12 *M* $HClO_4$	$1.35 \cdot 10^3$	[181]
Cystine-IO_3^-****	pH 9.46	$(1.83 \pm 0.12) \cdot 10^4$	[184]
Cystine-IO_4^-*****	pH 9.46	$(8.8 \pm 1.6) \cdot 10^4$	[184]
Mo(VI)—NO_3^-	0.05 *M* H_2SO_4	$2.5 \cdot 10^2$	[139]
Mo(VI)—NO_3^-	1 *M* H_2SO_4	$2.3 \cdot 10^2$	[139]
Cr(III)—NO_3^-	pH 5.0 at 0 °C	35	[202]
U(IV)—NO_3^-	pH 6	$7.9 \cdot 10^6$	[197]
Cu(II)—$S_2O_8^{2-}$	1 *M* KCl	$1.4 \cdot 10^3$	[206]
V(III)—V(IV)—H_2SO_4	pH 2	19	[209]
Y(III)-benzophenone	0.1 *M* $(C_2H_5)_4NClO_4$ in DMF	$(4.6 \pm 0.2) \cdot 10^3$	[27]
Y(III)-benzaldehyde	0.1 *M* $(C_2H_5)_4NClO_4$ in DMF	$(4.1 \pm 0.1) \cdot 10^3$	[27]
Y(III)-crotonaldehyde	0.1 *M* $(C_2H_5)_4NClO_4$ in DMF	$(2.5 \pm 0.3) \cdot 10^3$	[27]

*The rate constants for reactions involving oxidation by hydrogen peroxide were determined by a chemical method.

**The stoichiometric coefficient of the oxidation reaction was 5.5.

***The stoichiometric coefficient of the oxidation reaction was 6.

****The stoichiometric coefficient of the oxidation reaction was 3.

*****The stoichiometric coefficient of the oxidation reaction was 8. For the calculation of the oxidation reaction rate constant, it was necessary to divide k_{tot} by the corresponding stoichiometric coefficient of the oxidation reaction.

Notation: H_3Citr = citric acid; EDTA = ethylenediamine-tetra-acetic acid; PG = pyrogallol; CA = catechol; AA = ascorbic acid; BSED = bis-salicylidene-ethylenediamine; TEA = triethanolamine; NTA = nitrilotriacetate; SAL = sulphosalicylic acid; bipy = α,α′-bipyridyl; HA = hydroxylamine; SA = salicylic acid; H_2Trihydrox = trihydroxyglutaric acid; H_2Malic = malic acid; H_2Tartr = tartaric acid; H_2Malonic = malonic acid; H_2Glucar = saccharic acid; HGl = glycolic acid; H_2Tartron = tartronic acid; HMandelic = mandelic acid; HDPPA = α-hydroxy-α-dibutylphosphinoylpropionic acid.

Complex formation greatly influences the activity of the catalyst in the reduction processes, which also depends on the nature of the oxidant. Thus the activities of the Fe(II) and Ti(III) aquo-complexes in the reduction of H_2O_2 and NH_2OH are comparable, while the triethanolamine complexes of Fe(II) are more active by three–four orders of magnitude than the Ti(III) complexes (see Table).

The catalytic hydroxylamine waves are used in analytical practice mainly for the analysis of model solutions of niobium[101,102], ruthenium[103], tungsten[104,106], and the polarographically inactive CN^- ions[100].

3. The Catalytic Currents of Chlorate and Bromate Ions

Reactions involving oxidation by chlorates, bromates, iodates, perchlorates, and periodates are catalysed by variable oxidation state elements (molybdenum, osmium, etc.) (Kolthoff et al.[113], pp.97, 607), which can lead to the appearance of the catalytic currents of the above oxidants in the presence of transition elements. The ClO_3^- and BrO_3^- catalytic currents with participation of the transition elements of the first row, i.e. in the systems Ti(IV)–ClO_3^-–L,[114–132] Ti(IV)–BrO_3^-–L,[133–135] V(V)–BrO_3^-–L,[136] Fe(III)–ClO_3^-–L,[137] and Fe(III)–BrO_3^-,[138] with participation of transition elements of the second row, i.e. in the systems Mo(VI)–ClO_3^-–L [23,139–164] and Mo(VI)–BrO_3^-–L,[165,166] and with participation of the elements of the third row, i.e. in the system W(VI)–ClO_3^-–L [167] have been described in the literature. In addition a system involving a non-transition element, namely H_2SeO_3–ClO_3^-–L,[168,169] has also been described.

The catalytic ClO_3^- currents in the Ti(IV)–ClO_3^-–$H_2C_2O_4$–H_2SO_4 system were first investigated by Koryta and Tenygl[114], who established that 5.5 molecules of the titanium(III) complex participate in the reduction of ClO_3^- ions. The oxidation rate constant proved to be 1×10^4 litre mol^{-1} s^{-1}; this value was confirmed by many investigators[115–124].

Since the rate constants for the oxidation with chlorates of Ti(III) in $HClO_4$ and of the Ti(III) oxalate complex in H_2SO_4 are virtually equal (see Table), the Ti(III) aquo-ions are involved in the oxidation reaction responsible for the catalytic polarographic ClO_3^- current[126].

In the presence of an excess of oxalic (H_2Ox), citric (H_3Citr), and tartaric (H_2Tart) acids, EDTA, and CNS^- ions, titanium(IV) is reduced with a single reversible one-electron wave at less negative potentials than in the absence of the above ligands[39]. At low ligand concentrations a Ti(IV) reduction prewave is observed (catalysis by the ligand). In the presence of $KClO_3$ the height of both the aquo-ion wave and the prewave increases[124–126]. Among other acids, dicarboxylic acids comprising malonic acid (H_2Malonic) and carboxylic hydroxyacids comprising malic, trihydroxyglutaric (H_2Trihydrox), and glucaric (*d*-saccharic) acids also exhibit a catalytic activity (ligand catalysis). In the Ti(IV)–$KClO_3$–L systems the catalytic ClO_3^- current is superimposed on the Ti(IV) → Ti(III) reduction wave[127–132]. The current i_c is a maximum at pH 1–1.1, which can be explained by the involvement of the $Ti(OH)^{3+}$ species[127]. With increase of the $KClO_3$ concentration, the current i_c also increases and reaches a constant value, while with increase of the ligand content it passes through a maximum[124,125,127,128]. The catalytic waves in Ti(IV) solutions have the usual form with a distinct limiting current plateau and are described by the Koutecky theory[10].

The rate-limiting stages in the processes are the oxidation of $Ti(OH)^{3+}$ [125–127,130,132] or of its complex[128] by chlorate ions. At low ligand concentrations, where a prewave is observed, the mechanism of the generation of the catalytic current involves the oxidation of both the titanium aquo-ion and its complex ion[124,126], in which the organic ligands investigated exist in the form of uncharged species[125,132]. The ligands (see Table) can be arranged in the following sequence in terms of their increasing influence on the catalytic ClO_3^- current in the Ti(IV)–ClO_3^-–L system: H_2Malonic < H_2Malic < H_2Tart < H_2Citr < HDPPA < H_2Ox < Ph < H_2O < H_2Trihydrox < HMandelic ≪ CNS^-. The appreciable increase (by approximately four orders of magnitude) of the rate of oxidation of Ti(III)L on passing from an organic to an inorganic ligand (CNS^-) is probably associated with the faster formation of the complex $Ti(CNS)^{2+}$.[126]

The current i_c in the Ti(IV)–$KBrO_3$–EDTA system diminishes with increase of pH and at pH ≥ 3 reaches a constant value which is independent of the acidity of the solution[133].

As a representative of the titanium subgroup, zirconium does not give rise to a catalytic BrO_3^- wave in the presence of EDTA.[133]

In an acetate buffer solution at pH 5.0 the polarogram of vanadium(V) shows the catalytic BrO_3^- wave with a sharp maximum at $E = 0$ V,[136] which hardly changes after the introduction into the solution of 0.05 M resacetophenone oxime (2,4-dihydroacetophenone oxime), which forms a complex with V(V). The appearance of this wave is probably associated with the oxidation of the V(IV) formed by BrO_3^- ions to V(V), since it is located at the potentials of the V(V) → V(IV) reduction wave. The catalytic ClO_3^- and BrO_3^- currents in the Fe(III)–KCl system[137,138] are due to the interaction of ClO_3^- and BrO_3^- with the colloidal hydroxide $Fe(OH)_2$.

A large series of studies on the catalytic ClO_3^- currents in the presence of Mo(VI) have been carried out[23,139–164]. The first catalytic chlorate currents in the presence of Mo(VI) were investigated by Kolthoff and Hodara[139] at various sulphuric acid (0.01–2 M), sodium chlorate (0.2–1.2 M), and molybdenum(VI) concentrations. In weakly acidic H_2SO_4 solutions (up to 0.1 M) in the absence of chlorate, a single wave corresponds to the reduction of Mo(VI) to Mo(V) and two waves correspond to the reduction of Mo(V) to Mo(III). On the other hand, in strongly acid solutions ($c_{H_2SO_4} > 1$ M) the reduction of Mo(VI) to Mo(V) is characterised by two waves, while the reduction of Mo(V) to Mo(III) is characterised by a single wave, which can be explained by the reduction of various hydrolysed Mo(VI) and Mo(V) forms[140]. Two catalytic waves, due to the reduction by the Mo(V) and Mo(III) species of the chlorate ions formed at the electrode, are observed in the presence of chlorate. The rate of oxidation of Mo(III) to Mo(V) by chlorate, calculated from the data of Delahey and Stiehl[141], is independent of $c_{H_2SO_4}$.

In the presence of organic compounds (malic, tartaric, trihydroxyglutaric, mandelic[130], citric[144], glucaric[147], glycolic[148], tartronic[153], oxalic[145], and malonic[143] acids and catechol[149]), the Mo(VI) polarogram at pH 1.7 in the 0.1 M H_2SO_4 + 0.2 M Na_2SO_4 system consists of two or three waves. The catalytic wave in the form of a peak is located at the potentials of the first[143,144,147,149,153] or second[148] reduction wave of Mo(VI) and in oxalic acid solutions two peak-shaped catalytic waves, corresponding to the Mo(VI) and Mo(V) regeneration processes, are observed. In all cases the current i_c passes through a maximum with increase of the ligand concentration and the pH of the solution (pH_{max} 0.9–1.0). In the case of oxalic acid the heights of the first and second catalytic waves are maximum in 0.1 and 0.5 M H_2SO_4. With increase of c_{KClO_3} the current i_c increases in all cases and reaches a limiting value. The dependence of i_c on the acidity of the medium and other parameters can be explained by the different catalytic activities of the hydrolysed forms of molybdenum[23,145,161]. Many investigators[143–145,147–149,151–153] believe that the rate-limiting stage in the generation of catalytic currents is the oxidation of the molybdenum(V) complex by the chlorate ion. However, in some investigations[130,155] a coordination mechanism has been proposed, according to which the complex $Mo(V)L.ClO_3$ formed is reduced at the electrode.

The organic ligands investigated can be arranged in the following sequence in terms of increasing catalytic activity (see Table): $H_2O \ll H_3Citr < HGl < H_2Tart < H_2Malic < H_2Tartron < H_2Trihydrox < H_2Glucar < Ph \ll HMandelic$. A detailed study[23,161] of the catalytic currents in the presence of mandelic acid (the most active and the most readily sorbed ligand on the surface of mercury) showed that the catalytic currents are described by a mechanism in which the slow oxidation of various molybdenum(V) complexes incorporating the chlorate ion takes place on the surface of the electrode and not in the layer near it, as follows from Koutecky's theory[10].

In a study of the W(VI)–ClO_3^- system, where two catalytic peaks, observed in the presence of pseudotungstate, are due to the oxidation of $HW_6O_{20}^{3-}$ and $H_2W_6O_{20}^{2-}$, Hodara and Glasner[167] also concluded that the reaction responsible for the catalytic chlorate current occurs on the surface of the electrode; metatungstate does not exhibit a catalytic activity.

The joint influence of molybdenum(VI) and tungsten(VI) salts on catalytic ClO_3^- currents is of interest. The first catalytic ClO_3^- peak, due to the involvement of molybdenum(V), appreciably increases after the introduction of tungstate(VI) into the solution, which can be explained by the appreciable contribution of tungsten(V) to the catalytic activity of the heteropolyacid formed, which comprises tungsten(VI) and molybdenum(VI).[162]

On passing from titanium to molybdenum, the catalytic activity increases appreciably (see Table). The electrochemical reduction of BrO_3^- is catalysed by molybdenum(VI) in acetate buffer solution at pH 5.0. In the presence of resacetophenone isoniazid hydrazone the catalytic wave shifts towards more positive potentials and has the form of a peak with $E_p = -0.7$ V.[165] The authors[165] do not explain the generation of the catalytic BrO_3^- current.

The catalytic BrO_3^- current for selenium (a non-transition element) in solution at pH 2.5–4.0 is observed at the potentials of the second wave of selenium. It corresponds to the oxidation of H_2Se to zerovalent selenium[168,169] and obeys the Koutecky theory.

The catalytic chlorate currents have been used to determine ClO_3^- ions[114,129] and admixtures of titanium in trichlorosilane[121], in metallic aluminium of type Al 74[a], in steels[127,131,160], in natural waters and soil solutions[133,163], in rocks[158], in soils[159], in pure solutions[147,148,153], in technical sulphuric acid[164], and in tungsten[162]. Furthermore, the catalytic ClO_3^- currents are widely used in the determination of the polarographically inactive pyrogallol, salicylic and sulphosalicylic acids and catechol[123,125,149], and citric[124], glucaric[147], glycolic[148], tartronic[153], and mandelic[156] acids. Isopentyl alcohol, agar-agar[148], Tween 80,[153] and phenol[157] can be determined from the decrease of the catalytic current. Mandelic acid has come to be most widely used as the ligand for analytical purposes[158–160,163,164].

The catalytic bromate currents are used for highly sensitive determinations of titanium[133,134,135], vanadium[136], and molybdenum[165] (in solutions, and biological objects[166]) and of selenium[168,169].

4. Catalytic Currents of the Perchlorate Ion

In an acid medium perchlorates have a lower standard oxidation-reduction potential than chlorates, which is one of the causes of their low reactivity at room temperature. The catalytic perchlorate currents are therefore observed only for highly active catalysts such as molybdenum and tungsten. The catalytic ClO_4^- currents are not observed in the presence of titanium(IV) in view of the low rate of oxidation of titanium(III) by ClO_4^- ions; $k = 8.9 \times 10^{-2}$ litre mole^{-1} s^{-1} at 40 °C.[170]

The catalytic current in the Mo(VI)–ClO_4^- system has been observed by many investigators[139,171–180]. This phenomenon was first noted[171] in the polarography of Mo(VI) in $HClO_4$ solutions.

The formation of molybdenum(VI) and tungsten(VI) complexes with chloride ions[176,181] and carboxylic acids (tartaric, citric, and oxalic)[180] decreases i_c. Numerous mechanisms have been proposed for the catalytic current, according to which the current is due to the oxidation of Mo(IV) [174,175] or the reduction at the electrode of the complex Mo(V).ClO_4;[176] these mechanisms have been inadequately justified. We believe that the mechanism according to which the current is due to the oxidation of Mo(III) by perchlorate ions, proposed by Kolthoff and Hodara[139], is most correct. The catalytic current in the W(VI)–ClO_4^- system corresponds to the oxidation by perchlorate of the W(V) formed on the electrode[181].

The Table shows that the activities of molybdenum and tungsten in the catalytic reduction of ClO_4^- ions are approximately the same. The catalytic perchlorate currents make it possible to determine Mo(VI) at concentrations down to 1×10^{-6} M;[172–175] to increase the sensitivity of the methods, the solutions are polarographed at 40 °C [177] or time–current polarography is used[182].

The catalytic perchlorate currents have been used for analytical purposes in the determination of admixtures of molybdenum in iron and steels[182], in $HClO_4$,[170] in plants[173], in rocks[174,175], in various industrial and biological objects[177], and in soils[183].

5. Catalytic Currents of Iodate and Periodate Ions

Catalytic currents of iodate and periodate ions are observed in systems with sulphur-containing organic substances such as cystine[184], dithiocarbamate, and xanthate[24]. The ClO_3^-, BrO_3^-, NO_2^-, and H_2O_2 species do not exhibit catalytic effects in these organic systems. In the cystine–IO_3^-(IO_4^-) system the catalytic wave is combined with the first cystine reduction wave and has the form of a peak whose height is a maximum at pH 8.6–9.2. The current i_c can be greatly increased by the preliminary concentration of cystine at a stationary mercury microelectrode or by introducing ammonium or magnesium ions, which behave as activators[37].

The electrode process is described by the Koutecky theory and includes the oxidation of cysteine to the initial depolariser as the rate-limiting stage[185]. The introduction of IO_3^- at pH 7–11 into diethyldithiocarbamate (DTC) and ethyl xanthate (EX) solutions, which give rise to anodic polarographic waves, results in the appearance of a cathodic catalytic wave at potentials in the range between −0.5 and −0.6 V, which is much larger than the anodic wave and has the properties of surface waves[24]. The catalytic IO_3^- and IO_4^- currents make it possible to determine very low concentrations of sulphur-containing compounds: when cystine is initially concentrated at a stationary mercury microelectrode, its concentrations down to 10^{-8}–10^{-6} M can be determined[184].

The catalytic halogenate and perhalogenate currents tend to increase with increase of the number of the *d* orbital of the transition element (see Table). In catalysis by non-transition elements and organic substances, the catalytic current is observed only for bromate, iodate, and periodate. The rates of reduction of the substrates are then high and comparable to the rates characteristic of the Ti(IV)–ClO_3^-.(BrO_3^-)–organic ligand systems.

6. Catalytic Currents of Nitrate and Nitrite Ions

The catalytic currents of nitrate and nitrite ions are observed in the V(V)–NH_4Cl,[186] V(V)–EDTA,[187] Cr(III)–glycine[188], Cr(III)–EDTA,[189] molybdenum(VI),[139,177,180,190–195], and uranium(VI) [21,196–202] systems in various media. The catalytic currents for all the systems investigated are described by the Koutecky theory[10] and the reaction involving the oxidation of the depolariser reduction product by the nitrate or nitrite ion is rate-limiting. When the elements of the first transition series (vanadium and chromium) are used, V(II) or Cr(II) is oxidised to vanadium(IV) or chromium(III). The mechanism adopted is shown to be valid by the agreement between the rate constants for the Cr(II) oxidation reaction obtained by the chemical and polarographic methods[189].

The product of the reduction of NO_3^- by Cr(II) ions is NH_4^+.[189] The catalytic wave for the Mo(VI)–NO_3^- systems in acid sulphate[139,186,192], perchlorate[177], and chloride[192] solutions is located at the potentials of the Mo(V) → Mo(III) second wave and is due to the oxidation of Mo(III) to Mo(V). In contrast to nitrate ions, nitrite ions are involved in the oxidation of the Mo(V) formed to Mo(VI).[192]

The catalytic current in the U(VI)–NO_3^-(NO_2^-) systems is due to the oxidation of the U(III) formed to U(IV) [21,196–202] and the NO_3^- reduction product is hydroxylamine[203]. It has been established for the U(VI)–NO_3^- system[21] that the different signs of the charges of the reacting species exert an appreciable influence on the rates of the reactions responsible for the catalytic currents: the substrate has a negative charge and the catalyst has a positive charge. The rates of the NO_3^- or NO_2^- reduction reactions in the systems investigated (see Table) increase with increase of the number of the *d* or *f* orbital [sic], which is probably caused by the formation of labile systems capable of giving up electrons more readily on interaction with the oxidant.

The catalytic currents of nitrates are used for analytical purposes in order to determine the admixtures of molybdenum in technical and biological objects[177], in steels and reagents[193], in high-purity indium[194], in propene epoxidation products[195] and for the determination of uranium at very low concentrations, down to 1×10^{-8} M,[195–197,202] traces of uranium in rocks and untreated phosphates[201], NO_3^- and NO_2^-.[198]

7. Catalytic Currents of Persulphate Ions

The persulphate ion $S_2O_8^{2-}$ is reduced to SO_4^{2-} at positive potentials with participation of two electrons[39]. The specific adsorption of Br^- and I^- anions[204] or the formation of a sparingly soluble film of mercury iodide[205] have an inhibiting effect on its reduction. Chloride ions produce the same effect[206]. A catalytic wave, coinciding with the first copper(II) reduction wave, is observed in the Cu(II)–$S_2O_8^{2-}$–KCl system[206]. It is described by the Koutecky theory and is determined by the rate of oxidation of Cu(I) by persulphate ions with formation of Cu(II) and the SO_4^- radical-ion, which is consumed in the oxidation of Cu(I) or is reduced at the electrode. Interesting phenomena have been observed[207,208] in the study of the catalytic currents in the Cu(II)–$S_2O_8^{2-}$ system in 0.1 M $NaClO_4$ + 0.01 M $HClO_4$. A minimum arises on the polarogram in the presence of As(III) at $E = 0.1$ V, whose depth increases with increasing As(III), Cu(II), $S_2O_8^{2-}$, methanol, ethanol, and propanol concentrations and diminishes in the presence of acetonitrile, allylacetone, and Fe(III).[207] A minimum is also observed in the region of the reduction potential of the copper complex of EDTA (at $E \cong -0.5$ V) in $NaNO_3$ solutions containing 1 M ethylenediamine in the presence of As(III). To account for the results, a mechanism has been proposed in which the sulphate radical-anions formed are consumed in the oxidation of not only Cu(I) but also of As(III) and the other species investigated[207,208].

Catalytic Currents of Vanadium(IV)

In the generation of the catalytic oxygen currents described the oxidant-substrate is reduced at the electrode at much more negative potentials than the catalyst. However, there are systems in which part of the oxidant is reduced at the limiting current potentials of the catalyst wave and the oxidant reduction product is the catalyst itself, as, for example, in the V(IV)–V(III)–V(II)–H_2SO_4 system[209]. The polarogram of V(III) has a distinct diffusion wave with $E_{1/2} \cong -0.5$ V. When V(IV) is introduced, the V(III) reduction wave becomes indistinct and I_{lim} at the potentials corresponding to the V(III) diffusion current plateau exceeds the sum of i_d for V(III) and the V(IV) reduction current at this potential. The catalytic current is due to the oxidation of V(II) to V(III) by V(IV) ions. This process is accelerated by increase of pH in the range 0–1.3, which is due to the different oxidising capacities of the VO_2^{2+} and $V(OH).HSO_4^{2-}$ cations, which predominate under the given conditions. The catalytic currents, complicated by the reduction of the oxidant itself, are observed also in the Mo(VI)–V(V)–EDTA system at pH 4–6.[210].

In the Mo(VI)–V(V) mixture in the presence of EDTA, the three-electron molybdenum(VI) wave increases and the second vanadium(V) reduction wave, corresponding to the process V(IV) → V(III), disappears, which can be explained by the involvement of V(V) ions in the catalytic Mo(III) oxidation reaction[210]. However, it is difficult to agree with this, since the potential corresponding to the reduction of the complex V(V).EDTA to V(IV).EDTA is more positive by ~0.7–0.8 V than the reduction potential of molybdenum(VI). The involvement of V(IV) complexes as the oxidants is most probable. The V(IV) catalytic currents, observed in the U(VI)–V(IV) system[211], are used to determine low uranium concentrations.

9. Catalytic Currents of Sulphuric and Certain Carboxylic Acids

The limiting reduction currents of sulphur dioxide, bromine, and iodine against the background of concentrated sulphuric acid are catalytic in nature[212] owing to the oxidation of the electrochemical reduction products of these depolarisers to their initial state by sulphuric acid.

Among carboxylic acids, oxalic and glyoxylic acids are known as oxidant-substrates[213]. Oxalic acid is reduced to glyoxylic acid at the mercury dropping electrode[214]. In the presence of uranium(VI) the reaction takes place at more positive potentials with formation of glycolic acid[213]. Under these conditions, the catalytic wave of oxalic acid coincides with the second uranium(VI) reduction wave: $UO_2^+ + 2e \rightarrow U(III)$. The same catalytic wave is observed also in the presence of glyoxylic acid. The catalytic reduction currents of the above acids are due to their reaction with U(III) to form glycolic acid and U(IV). The latter is reduced electrochemically to U(III) and the reactions described are then repeated[213].

The catalytic currents in the U(VI)–glyoxylic acid system can be used to determine U(VI) and glyoxylic acid[215].

III. THE FIXATION OF ATMOSPHERIC NITROGEN—A POSSIBLE APPLICATION OF THE CATALYTIC CURRENTS OF SUBSTRATES

The intensive development of agriculture requires the use of considerable amounts of inorganic fertilisers. Thus, from 1st July, 1938 to 30th June, 1939, 9.2×10^6 tonnes of nutrient elements were produced in the world in terms of N_2, P_2O_5, and K_2O,[216] while in the period 1977–1978 the corresponding figure was 106.1×10^6 tonnes, including 40.9×10^6 tonnes of N_2.[217] The present capacity of the world nitrogen industry meets less than 10% of the requirements of agriculture for nitrogen fertilisers[218].

The industrial methods of producing bound nitrogen are energy consuming and are carried out at high temperatures and pressures, while the enzymic fixation of nitrogen† takes place in nature under very mild conditions. Consequently, the fixation of atmospheric nitrogen under mild conditions is possible in principle and the development of industrial fixation methods is an urgent problem in modern chemical science.

The fixation of atmospheric nitrogen under mild conditions is a reaction catalysed by electron-transfer reagents[219]. It is therefore interesting to consider them under the conditions of the electrochemical regeneration of mediators, together with the catalytic currents of molecular nitrogen as the substrate. The non-enzymatic fixation of nitrogen under mild conditions was first described by Vol'pin and Shur[220]. Numerous studies (surveyed in reviews[221–224]) on this question were published over a short period.

Thermodynamically feasible nitrogen fixation reduction processes are difficult because in the dissociation of the triple bond in the N_2 molecule most of the energy (131 kcal [225] out of 225 kcal [226]) is consumed in the rupture of the first bond. In the direct reduction one must therefore use particularly powerful reductants. The formation of complexes of nitrogen molecules with transition elements[227,228] makes it possible to distribute more uniformly the dissociation energy of the π-bonds in the N_2 molecule among separate stages.

Nitrogen can be reduced stepwise with participation of two, four, and six electrons, leading to the formation of N_2H_2, N_2H_4, and NH_3. The four-electron process, involving the reduction of nitrogen to hydrazine, is energetically most favourable[222]. The N_2–reductant (transition element and others) system under the conditions of the electrochemical generation of the reductant resembles the systems already considered, in which the catalytic currents of oxidant substrates are observed. One cannot therefore rule out the possibility that the study of the oxidant catalytic currents, including the molecular nitrogen current, may lead to the refinement of the mechanism of the nitrogen fixation process or may lead to the discovery of new principles for the selection of nitrogen-fixing systems "working" under mild conditions.

Vol'pin and Shur[220], who observed the fixation of nitrogen at room temperature also in aprotic (etheral and hydrocarbon) media, used powerful reductants such as $LiAlH_4$, C_2H_5MgBr, and (iso-C_4H_9)Al. Nitrogen fixation was observed in the presence of transition metal salts ($CrCl_3$, $MoCl_5$, WCl_5, $FeCl_3$, and $TiCl_4$). Ammonia was evolved in the hydrolysis of the products formed. Many investigators whose studies have been surveyed[221–224] used transition elements (V, Mn, Co, Zr, Ru, Os, and Nb), apart from the elements in the above salts, as catalysts and the reductants were alkali, alkaline earth (Mg) and lanthanide (La and Ce) metals, alkali metal naphthalides and hydrides[219,222–224], and sodium amalgam[229]; electrochemical reduction has also been employed[230–234]. As expected, hydrazine and ammonia were obtained in the hydrolysis of the products of the nitrogen-fixing systems. In the systems investigated the transition elements played the role of catalysts or, in rare instances, the role of both catalysts and reductants [for example, in the V(II)–Mg(II)–N_2 system[235,236]]. The catalytic effect of the transition element is manifested under a rigorously specific combination of conditions: the standard potential of the reductant must be greater or equal to the potential of the catalyst and greater than the potential of hydrazine; the reductant must exhibit a specific activity in relation to nitrogen[222].

Under the conditions investigated, the nitrogen activation stage consists of the formation of the dinuclear complex MN_2M,[237] in which the transition element M is in the d^1 or d^3 state. In subsequent steps electrons are transferred from the reductant to the activated nitrogen. This mechanism is identical with that of the catalytic reduction of nitrogen in biological processes catalysed by nitrogenase[219,222] and other enzymes[238,239]. In electrochemical systems the cathode is a universal reductant, at which one can establish any potentials for the reduction of substances, including molecular nitrogen. It is not therefore fortuitous that investigators have resorted to electrochemical methods[230–234], including polarography, to study the fixation of nitrogen.

The fixation of molecular nitrogen has also been studied by the molecular orbital (MO) method in relation to reactions in the $[N_2 + H]^{\cdot}$, $[N_2 + H^{\cdot}]^+$, and $[N_2^- + H^{\cdot}]^-$ model systems[240].

The nitrogen fixation mechanism presented above can ensure the appearance of the catalytic polarographic current of nitrogen. The behaviour of the nitrogen-fixing systems V(II)–catechol[241] and Mo(III)–Mg(II)–Na(Hg) [242] has been studied. The lack of literature data for the catalytic polarographic currents of molecular nitrogen as the oxidant-substrate in nitrogen-fixing systems is probably associated with the fact that the rate of oxidation of the intermediate transition metal complex by molecular nitrogen is not high enough to be appreciable under polarographic conditions. However, in principle, it will be possible to observe the catalytic polarographic current of molecular nitrogen under certain conditions and to use it as an indicator for the selection of nitrogen fixation conditions.

Thus transition and certain non-transition elements are used as catalysts of the reactions responsible for the catalytic polarographic currents of substrates. The catalytic activity of an inorganic catalyst increases with the number of its *d* orbital. Complex formation in most cases leads to an increase in activity of the catalyst, but sometimes the opposite phenomenon takes place.

The maximum activities of many catalysts are observed at pH values close to the p*K* for their hydrolysis, which can be used to estimate the activities and the degrees of involvement of various hydrolysed forms of catalysts in the catalytic process.

The properties of oxidant-substrates are shown by H_2O_2, ClO_3^-, BrO_3^-, IO_3^-, ClO_4^-, IO_4^-, NO_2^-, NO_3^-, NH_2OH, V(V), V(IV), $S_2O_8^{2-}$, H_2SO_4, $H_2C_2O_4$, COHCOOH, and saturated compounds, organic halogeno-compounds, sulphur-containing compounds, and amino-compounds. The strongest oxidants can be arranged in the following sequence in order of increase of their reactivity. $ClO_4^- < NH_2OH < NO_2^- < NO_3^- < H_2O_2 < S_2O_8^{2-} < IO_4^- < IO_3^- < BrO_3^- < ClO_3^-$ (see Table).

The generation of catalytic currents is in most of the cases examined due to the oxidation of the reduced form of the catalyst by the substrate in the layer near the electrode or

†By the fixation of nitrogen, we understand a process involving the complete or partial rupture of the N≡N bond.

on the electrode surface. In systems with hydrogen peroxide one cannot rule out the possibility of the reduction at the electrode of the substrate bound in a complex with one of the forms of the catalyst.

The catalytic currents have found extensive applications in analytical practice for the analysis of admixtures of the catalyst, substrates, and polarographically inactive substances forming complexes with the catalyst, and also in the study of complex formation. One cannot rule out the possibility of using the catalytic currents also in the study of the molecular nitrogen fixation processes under mild conditions.

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Electrochemistry of Iodine

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The results of studies of redox processes in systems which include iodine are generalised. The adsorption of iodine on metals is discussed, and the relationship between the type of adsorption and the electrode reactions of the iodine is examined. 190 references.

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I. SPECIFIC ADSORPTION OF IODIDE IONS

The adsorption of iodide ions on different electrodes from different media has been fully investigated[1-72]. The main aim of that work was to determine the structure of the electrical double layer (EDL) and, in particular, the effect of the specific adsorption of the ions on various electrode processes (metal dissolution, hydrogen evolution, etc.). In this Section we shall attempt to generalise (qualitatively) data on the adsorption of iodide ions on metals in order to explain the general features of the adsorption: this is an essential preliminary to any discussion of the kinetics and mechanism of the redox reactions of iodine.

The rate of an electrochemical process is strongly dependent on the structure of the EDL, which is determined by the nature of the adsorption of the reacting ions on the electrode surface. The adsorption type (especially in the case of specific adsorption) depends on the one hand on the stability of the complexes (or chemical compounds) formed by the adatoms (or ions) with the surface atoms of the metal electrode at the ψ' potential[1], and on the other hand it depends on the primary hydration (or solvation) number[2] of the ion in the bulk of the solution. The adsorption of iodide ions from different media and on different electrodes is determined by these factors.

On mercury electrodes[3-7] the adsorption of iodide ions causes an increase in the capacity of the EDL,[3] an anomalous change in zero-charge potential with the logarithm of the concentration of I^- (the Esin–Markov effect),[5] a lowering of the electrocapillarity maximum (accompanied by a negative shift)[1,3], a decrease in hydrogen evolution overvoltage (η_{H_2}) in acid solutions[4,7] a linear decrease in heat of adsorption with increase in surface coverage[6], and a shift of the ψ' potential towards more negative values[4,7]. If the formation of the surface compound results in a full (or partial) loss of charge by the iodide ions the EDL capacity should decrease, and conversely if as a result of the low stability of the surface complex the iodide ions accumulate in the fixed part of the EDL the capacity should increase.

The negative shift of ψ' (which lowers η_{H_2}) and the increase in capacity suggest a weak chemical interaction between Hg and I^-. In this case the I^- anions are adsorbed in the ionic "condenser plate" of the EDL, where they generate a negative ψ' potential and (according to the slow discharge theory) they increase the rate of evolution of hydrogen. However, it has been shown experimentally[8] that the negative shift of ψ' is not accompanied by an accumulation of H^+ ions on the mercury surface: this suggests[8] that the influence of I^- and other anions on this electrode is not primarily the ψ' effect but a substantial lowering of the activity coefficient of the activated complex. Another important factor on the mercury electrode is the mutual repulsion of the I^- ions chemisorbed on the surface, i.e. the high mobility of these ions on the uniform mercury surface[6].

There can be no doubt that the number of ions in the EDL depends on their degree of solvation (hydration) in the solution. Hence the observed sequence of specific adsorbability ($Cl^- < Br^- < I^-$) from water solutions, which applies to almost all metals, is invariably ascribed to decreasing hydration. In contrast to their behaviour in protonic solvents (water, methanol, acetic acid, etc.), iodide ions are easily solvated in dipolar aprotic solvents such as dimethylformamide (DMF), dimethylsulphoxide (DMSO), acetone, and acetonitrile[9]. This difference is sharply reflected in the specific adsorption of I^- at the mercury–electrolyte interface with non-aqueous solvents. For example, the surface activity of iodide anions at the mercury–DMF interface is lower than at the mercury–water interface[10,11,14], and the lowering of surface tension caused by the adsorption of I^- on an uncharged mercury surface in water is greater than in DMF.[10] The difference is even more marked if we compare water with formamide[10].

Damaskin and coworkers[10,11] ascribe this effect to competition between the adsorption of I^- anions and the adsorption of solvent molecules. Obviously, we must again allow for the strong solvation of I^- in aprotic solvents, since the difference in solvation energy of the anions decreases in the series from Cl^- to I^- in water, but increases in DMF.[11] The free energy of adsorption of I^- on an uncharged mercury surface from aqueous solutions is 37.1 kcal mole^{-1}, as compared with 29 kcal mole^{-1} for solutions in DMF under the same conditions. In comparison with the mercury–water interface, the mutual repulsion of specifically adsorbed anions is stronger at the mercury/DMF,[11] mercury–*N*-methylformamide (MFA),[12] mercury/formamide[15], and mercury/DMSO interface[13,16]: this is shown by the decrease in the second virial coefficient (B) when DMF is replaced by water.

Under certain conditions even organic surface-active ions have very little effect on the adsorption of I^- on mercury[7,17].

On iron, cobalt, and nickel. In contrast to its adsorption on mercury, the adsorption of I^- on solid metals (especially Fe,[18-24] Co,[25,26] and Ni [27-29]) is due to the formation of a strong M–I^- chemical bond. Iodide ions chemisorbed on an iron surface[18,19,21] have a passivating effect on the metal: η_{H_2} is increased[19,22], and the ionisation reaction is suppressed[20]. The capacity of the iron electrode decreases more

than two-fold in the presence of even very small amounts of KI (0.002 *N*), the additional decrease caused by increasing the KI concentration to 0.2 *N* being almost negligible[21]. The decrease in capacity increases with the concentration of H_2SO_4 (from 1 to 8 *N*).[21]

The maximum number of iodide ions adsorbed on Fe has been shown by a radioactive tracer method to be 4×10^{-10} g-atom cm^{-2}, corresponding to 50% coverage of the iron surface. Therefore it is generally thought that the passivating effect of I^- on Fe cannot be due to the formation of a surface compound. However, the lowering of the double layer capacitance of Fe from 33–35 μF cm^{-2} (in 1 *N* H_2SO_4) to 10–15 μF cm^{-2} by the addition of 0.001 mole $litre^{-1}$ of KI conclusively proves that iodide ions are chemisorbed[21]. It is interesting to note that the capacity of iron in sulphuric acid is unaffected by the presence in solution of an organic surface-active ion (the tetrabutylammonium cation), whereas addition of iodide ions to the same solution causes a marked decrease (to 7–10 μF cm^{-2}) in the capacity of the electrode[19]. This is explained by the formation of dipolar Fe–I^- molecules with their negative end pointing towards the solution, which assists the adsorption of positively charged species. The Fe–I^- surface complex is stable only in acid solutions[24].

It has also been shown that halogens adsorbed on Fe retain some excess negative charge, though not to the same extent as in the adsorption on mercury[22]. Oshe even suggests[23] that the halide ions can penetrate into the surface layer of the the iron and perturb the crystal structure.

Halide ions adsorbed on cobalt[25,26], as on iron, increase the overvoltage of both the cathodic process (discharge of hydrogen ions) and the anodic process (cobalt ionisation reaction). Increasing i_a and ϕ_a accelerates the removal of the adsorbed ions (together with the ionised surface atoms of the cobalt electrode[26]).

Iodide ions weaken the Ni–H bond: they displace adsorbed hydrogen atoms from the surface and they raise η_{H_2}, the magnitude of the effect increasing with the concentration of I^- in solution[27,28]. At low concentrations of I^- ($\lg c_{I^-} < -4$) the differential capacity of nickel decreases as the concentration of I^- increases due to increasing chemisorption of I^-. Further increase in the concentration of I^- brings less strongly bound I^- ions into the surface layer, and the capacity begins to rise[29].

On lead and tin. The adsorption of iodide ions on lead[30–34] takes place in two steps. Kolotyrkin and coworkers[30] have shown that the first step consist in the (fast) penetration of the anions into the EDL, accompanied by an increase in capacity. In the second (slow) step a strengthening of the bond between the anions and the surface metal atoms takes place, and the capacity decreases. In acid solutions an increase in the concentration of KI from 1×10^{-5} to 1×10^{-3} *N* increases the coverage of the lead electrode surface with iodide ions from 0.37 to 38.5% of a monolayer. At low coverages (0–15%) and increase in the number of adsorbed iodide ions lowers η_{H_2}, whereas at coverages greater than 15% the effect is the opposite: in this case an increase in adsorption produces a marked increase in η_{H_2}, to a level higher than the overvoltage in pure acid solutions when the coverage exceeds 30% of a monolayer.

The surface excess of specifically adsorbed I^- for the same total density of charge is lower on lead than on mercury[32]; the shift in the zero-charge potential caused by iodide anions is greater on mercury than on lead[31,33]; the minimum on the $c-\phi$ curve occurs at 10^{-5} *N* KI concentration on mercury[3], whereas on lead[31] (and on tin[37]) it occurs at 10^{-3} *N* KI. Thus it appears that the specific adsorption of I^- is weaker on lead than on mercury. A generalised model of the EDL [34] can be used to calculate the change in η_{H_2} on lead caused by the adsorption of I^-.

On cadmium and thallium. On a cadmium and a thallium electrode[30,35], as on a lead electrode, the positive swing in potential caused by I^- ions produces first a lowering and then a rise in η_{H_2}. The adsorption of water dipoles with their negative end towards the electrode surface is more marked on a cadmium than on a lead electrode[36]. The relative values of the energy of adsorption of the iodide ion on cadmium ($\Delta G^0_{I^-} = -22.0$ kcal $mole^{-1}$) and on mercury (−37.1 kcal $mole^{-1}$) are consistent with the surface excesses of iodide ions on the two metals, and show that the iodide ion is adsorbed less strongly on cadmium than on mercury[36].

On silver. The adsorption of I^- anions on the (100) face of silver single crystals is stronger than on any other solid electrode[38]. This is explained by the extremely low solubility in water of the silver halides[39,40], which causes a substantial (2–3-fold) decrease in the differential capacity of the EDL,[40] as in the case of iron. Unlike the adsorption on Pb, the adsorption of I^- on Ag causes only an increase in η_{H_2} over a wide range of KI concentrations (from 10^{-9} to 10^{-3} g-equiv $litre^{-1}$).[40]

The potential corresponding to full adsorption varies substantially with the pH of the solution. An increase in pH at constant potential always produces a marked decrease in adsorption: the effect is strongest in acid solutions (pH < 6), whereas in strongly alkaline solutions the effect of pH on the adsorption is much weaker[40].†

Because of the very low coverage of the silver surface by adsorbed ions (~10% of a monolayer[39]) the penetration of I^- into the metal lattice is thought[40] to be unlikely. However it has been shown[42,43] that the adsorption of I^- on Ag is accompanied by penetration into the metal lattice as a result of the relatively fast exchange with surface atoms of silver.

On bismuth. The adsorption of I^- on bismuth[44–47,50] is lower than on mercury, but somewhat higher than on Pb [31] and Cd.[35] However, the surface activity of the iodide ions, i.e. the magnitude of the negative shift of the minimum in the ε,ϕ curve, is lower for Bi and In than for Pb and Tl.[51]

At low concentrations of KI (<10^{-2} M) the shift in the zero-charge potential for the (111) face of a bismuth single crystal is smaller than for the surface of a cast bismuth ingot, but at higher concentrations of KI (>10^{-2} M) the shift becomes greater for the monocrystalline than for the polycrystalline surface. The repulsion between specifically adsorbed I^- anions on a (111) face with $\varepsilon < 0$ is substantially higher than on the polycrystalline face, but with $\varepsilon > 0$ the opposite is true. On a cast bismuth electrode the enhanced specific adsorption is accompanied by closer approach of the inner Helmholtz plane to the electrode surface[44].

The adsorption of I^- on Bi is stronger from aqueous than from methanolic solutions[48,49], increasing more rapidly with the concentration of I^- in water than in methanol solutions. Changing from water to methanol solutions of I^- causes the planes of the EDL on Bi to move apart[48]. The increase in the distance from the outer Helmholtz plane to the surface (x_2) in methanol is accompanied by a strong (2–3-fold) enhancement of the repulsion between adsorbed ions, caused by the closer approach of the inner Helmholtz plane (x_1) to

†A similar pH effect is observed in the adsorption of I^- on Cu, Au, Pt, Ni, and stainless steel. On the other hand on glass the adsorption of I^- increases significantly with pH.[41]

the electrode surface with increasing adsorption of the iodide ion[49]. The standard free energy of adsorption $\Delta G^0_{I^-}$ on Bi is -23.9 kcal mole^{-1} from aqueous solutions and -25.6 kcal mole^{-1} from methanolic solutions[48]. The increase in $\Delta G^0_{I^-}$ on changing the solvent from water to methanol is due essentially to the lower solvation of the anions in the latter medium, but there is also an effect from the change in interaction energy of the solvent molecules adsorbed on the Bi.[48,49]

The adsorption of I^- is weaker on Bi than on Hg even when ethylene glycol is used as the solvent[52]. However, and in contrast to aqueous, methanolic, and ethylene glycol solutions, in DMF [53] and DMSO [54] solutions the surface concentrations of specifically adsorbed anions are almost identical on Bi and Hg. The orientation polarisation of the DMF dipoles increases in the series $Cl^- < Br^- < I^-$, as does also the solvation energy of the halide ions in DMF.[53] The specific interaction of the solvents with the uncharged bismuth surface decreases in the sequence DMF > DMSO > $H_2O \geq CH_3OH \geq$ acetonitrile, and the ratio $(x_2 - x_1)/x_2$ which characterises the approach of the inner Helmholtz plane to the electrode surface increases as follows when I^- is adsorbed on Bi from different solvents: $H_2O <$ acetonitrile < DMSO = ethanol < methanol < DMF.[53]

On gallium the adsorption of I^- is also less than on mercury, but the M–I^- bond is stronger on gallium than on mercury[55]. The increase in η_{H_2} due to the presence of I^- is more marked on a solid than on a liquid gallium electrode[56]. When gallium is melted in solutions of sulphuric or perchloric acid containing iodides the overvoltage η_{H_2} immediately falls to the level for a liquid electrode in the same solution. If the gallium is re-frozen in the same solution η_{H_2} increases (more slowly) to the limiting value η_{lim}. Solidification of the gallium strengthens the bond between the halide ions and the metal, and the effect increases with time, suggesting a continuing expansion of the crystal lattice in solid gallium[56].

The increase in EDL capacity accompanied by a shift of ϕ towards less negative values was explained by Frumkin[55] not in terms of anion adsorption, though it must play a part (even if only minor), especially in the case of I^- ion, but in terms of the adsorption of water molecules on the gallium. It is interesting to note that on high-purity gallium (99.9998–99.9999%) the addition of halide anions raises η_{H_2},[57] whereas on gallium of 99.996% purity halide ions lower η_{H_2}.[58]

On platinum. On smooth platinum the adsorption of I^- from a 1 *N* H_2SO_4 + 0.01 *N* KI solution is 1.5×10^{-9} g-ion cm^{-2} of apparent surface, i.e. close to the number needed to form a complete monolayer[59]. Incomplete coverage of the platinum surface has been reported[60,61]. The maximum adsorption of iodide ions on platinised platinum (at $\phi = 0.4$ V) is 3.7×10^{-9} g-equiv cm^{-2}; for smooth platinum under the same conditions an adsorption of 6.5×10^{-8} g-equiv cm^{-2} was obtained (i.e. ~20 times greater than on platinised platinum when calculated for a uniform surface)[61]. However, 2–2.5 times more hydrogen is desorbed from smooth than from platinised platinum.

The difference in adsorption capacity between smooth and platinised platinum is ascribed[61] to faults in the lattice of smooth platinum resulting from its technological surface treatment. The increased irreversibility of the adsorption of iodide on platinum, and the decreased adsorption and increased desorption at higher temperatures, are ascribed[61] to the penetration of the adsorbed particles into the underlying layers of the metal. Hydroxyl ions suppress the adsorption of iodide on platinum at all potentials more negative than 1.0 V with respect to the NHE.[59] At high anodic potentials (the oxygen evolution potential) in alkaline solutions, however, the adsorption of iodine is substantial and well in excess of several monolayers of I^-. This is explained by the formation of a stable chemical compound between iodine and the platinum oxides produced under those conditions. The surface compounds are easily soluble in acids, but they are stable in alkaline solutions even under cathodic polarisation[59]. However, it is pointed out[62–64] that I^- (unlike I_2 [62]) is not adsorbed on an oxide-covered platinum surface.

It has been reported[65,66] that in the iodide–iodine–iodide/iodine complex system the species adsorbed on platinum is not I_3^- but I_2 (or iodine atoms), and that the adsorption of I_2 is far greater than that of I^-. The double mechanism (reversible, or irreversible) of the adsorption of I_2 and I^- on platinum[65,66] should also be noted: I_2 is adsorbed irreversibly on the part of the platinum surface which is free from adsorbed iodide, whereas on the regions covered with I^- or with irreversibly adsorbed I_2 the further adsorption of I_2 is reversible. Thus the irreversibly adsorbed state includes I_2 as well as I^-.[63,65] Of the various oxidised forms of iodine the most strongly adsorbed is I^-, even to the extent of displacing other adsorbed ions or molecules[63,64]. This explains the steep drop in the EDL capacity of platinum and in the electrical conductance of the platinum–solution interface, the decrease in the amount of adsorbed hydrogen, and the decrease in the energy of its bond to the platinum surface in the presence of I^-.[59,60,67,68]

On palladium, rhodium, and iridium. The main features of the adsorption of I^- on Pd,[69,70] Rh,[71] and Ir [72] are described by the logarithmic Temkin isotherm and Roginskii–Zel'dovich equation. The adsorption of I^- on palladium[69] produces a new phase of the compound PdI_2. In the ϕ region where the formation of compounds between I^- and the metal is inhibited the I^- ion exists at Pd–I^- dipoles. Pd and Rh surfaces, like Pt surfaces, acquire a greater positive charge in NaI solutions than in NaBr. On Rh, as on Pt, the coverage of the surface by iodide increases rapidly at first and then more slowly[71]. On rhodium the I^- cannot compete with oxygen for surface sites[71]. As on Pt,[61] and on Pd,[69] partial charge transfer from I^- to the electrode takes place on Ir.[72]

The metals of the platinum group can be arranged in the following order of decreasing displacement of adsorbed hydrogen by iodide ions: Rh > Ir > Pt > Pd. The slope of the I^- adsorption isotherms for metals of the platnium group is thought[71] to be determined by the simultaneous effect of two distinct factors: the nature of the surface non-uniformity and the mutual repulsion forces between anions.

Thus the adsorption of iodide ions on different electrodes is essentially chemical in nature. However, a number of features are inconsistent with this statement: a) full coverage of the metal surface by adsorbed ions is only exceptionally observed; b) the adsorption of I^- on Cd, Pb, Ga, and Bi is smaller than on Hg, and the adsorption on Ag and Pt is greater than on Hg, in spite of the fact that the energy of formation (in kcal mole^{-1}) of the compounds PbI_2 (41.85), CdI_2 (48), and GaI_3 (51.2) is much higher, and that of AgI (14.91) and PtI_4 (21.6) is much lower, than the energy of formation of HgI_2 (25) or Hg_2I_2 (29);[73,74] c) the radius of the Pt atom (1.38 Å) or of the Pt^{2+} ion (0.93 Å) is almost one-half the radius of the I^- ion (2.2 Å),[75] and therefore the formation of compounds of the PtI_2 (and especially the PtI_4) type on the surface of Pt seems unlikely.

The metals can be arranged in the following sequence of increasing adsorption of I^-: Cd (−0.402) ≅ Tl (−0.336) < Sn (−0.140) ≅ Pb (−0.126) < Ga (−0.520) < Bi (+0.200) < Hg (+0.788) < Co(−0.277) ≅ Ni (−0.25) < Fe (−0.036) < Ag (+0.799) ≅ Rh (~+0.8) ≅ Pd (+0.987) ≅ Ir (+1.00) < Pt (~+1.200). The numbers in brackets are the standard redox potentials (in volts) of the metals in aqueous solutions[75]. The adsorption of I^- increases as the standard potential becomes more positive, with gallium and the elements of the iron family as the only exceptions. Hence we may assume that the adsorption of I^- on metals is not purely chemical, but physicochemical in nature, i.e. dependent on the charge of the metal surface. This hypothesis is consistent with the finding[76] that the standard free energy of adsorption of I^- on mercury is linearly related to the positive charge on the electrode.

The sharp drop in EDL capacity caused by the adsorption of I^- on solid metals and the associated (partial, or full) charge transfer from the I^- to the metal[77] (especially on metals with a strongly positive surface charge) can be explained by the distortion of the outer electron clouds of the adsorbed ions, resulting in a deviation from a discrete distribution in the case of a solid electrode (in contrast to the mercury electrode).

II. STANDARD AND EQUILIBRIUM POTENTIALS IN SYSTEMS WHICH INCLUDE IODINE

The equilibrium potentials of the I_2/I^- system, for the overall electrode reaction

$$2I^- - 2e \rightleftarrows I_2 , \qquad (1)$$

and of the I_3^-/I^- system, for the overall electrode reaction

$$3I^- - 2e \rightleftarrows I_3^- , \qquad (2)$$

are given by the Nernst equation[78-80]

$$\varphi_{(1)} = \varphi^0_{(1)} + (RT/nF)\ln([I_2]/[I^-]^2) , \qquad (3)$$

$$\varphi_{(2)} = \varphi^0_{(2)} + (RT/nF)\ln([I_3^-]/[I^-]^3) . \qquad (4)$$

In these expressions n is the number of electrons in the overall electrode reaction, and F is the Faraday. The standard electrode potentials (in V) of the I_2/I^- system in aqueous solutions are 0.621 [81-83] or 0.628 [82,84] with I_2(aq), and 0.535 [83,85] or 0.536 [82] with I_2(s), whereas those for the I_3^-/I^- system are 0.536 [81-83,85] or 0.545.[82,84]

In Eqns.(3) and (4) the pre-logarithmic factor is the same for reactions (1) and (2), since $n = 2$ in both cases, and is a function of temperature only: $\partial\phi_p/\partial \ln([I_2]/[I^-]^2) = \partial\phi_p/\partial \ln([I_3^-]/[I^-]^3) = 0.02958$ at 25 °C.[79]

Increasing the concentration of I^- in solution converts the iodine into the iodine–iodide complex (I_3^-), and the equilibrium potential depends not only on the activity of I^- but also on the activity of I_3^-. At constant concentration of I_3^- the equilibrium potential of the I_3^-/I^- system decreases exponentially with the concentration of I^-:

$$\varphi_p = \varphi_0' - (RT/nF)\ln[I^-]^3 = \varphi_0' - (3RT/2F)\ln[I^-] . \qquad (5)$$

Assuming that the electrode reaction is described by Eqn.(1), at constant I_2 concentration the rate of decrease of the electrode potential with increasing I^- concentration is described by the equation

$$\partial\varphi_p/\partial \ln[I^-] = -(RT/F) .$$

At low and constant concentration of iodine[78], or when no iodine is present in the initial solution[80], the experimentally observed decrease in ϕ_p with increase in I^- concentration corresponds to Eqn.(5), i.e. the equilibrium in the system is described by Eqn.(2). This assumption is confirmed by the temperature dependence of the equilibrium potential, i.e.[80]

$$\partial\varphi_p/\partial T = -3R(\ln[I^-])/2F .$$

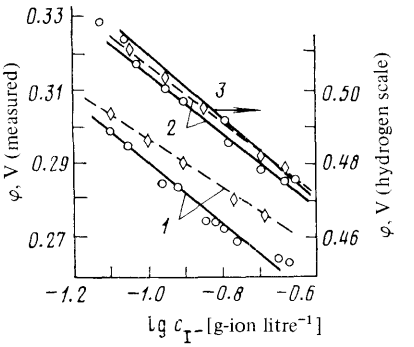


Figure 1. Equilibrium potential ϕ_p against logarithm of the concentration of iodide ions on platinum (*1*, *2*) and on graphite (*3*) in the presence (broken lines) and in the absence (full lines) of naphthenic acids[80]: *1*) and *3*) without supporting electrolyte, *2*) in the presence of 1 *N* Na_2SO_4.

At all concentrations of I^- the platinum[78,80] and the graphite[80] electrode have a positive potential (Fig.1), due to the dipole in the Pt–I^- bond[59], and the potential changes are caused not only by changes in surface coverage but also by changes in the electrode–adsorbate interaction energy[51] and changes in the dipole moment of the platinum–iodide bond brought about by the increased strength of the bond[59].

The equilibrium potential of platinum becomes more positive in the presence of 1 *N* Na_2SO_4 (Fig.1), evidently as a result of a change in state of the I^- in the outer Helmholtz plane (i.e. of a change in the ψ' potential)[80]. Naphthenic acids also cause a positive shift in the potential of platinum in iodide solutions (Fig.1).

On a tellurium[86] and a zinc[87] electrode in aqueous solutions the equilibrium potential corresponding to the following reactions is rapidly established:

$$TeI_6^{2-} + 4e \rightleftarrows Te + 6I^-$$

$$ZnI_3^- + 2e \rightleftarrows Zn + 3I^- .$$

The standard I_2/I^- potentials decrease as the concentration of acetic acid increases in $CH_3COOH + H_2O$ mixtures: the effect amounts to 200 mV for a change in concentration from 0 to 80% CH_3COOH.[88] This dependence of the standard potential of the I_2/I^- system on the concentration of acetic acid cannot be explained by an increase in the stability of I_3^-, since this complex raises the potential of the system [see Eqn.(4)].

The standard redox potentials (in V) are:

Solvent	Nitromethane	Acetone	Acetonitrile	DMF	CH_3COOH
I_3^-/I^-	0.11 [82,90]	0.11 [82,90]	0.06 [82,90]	−0.37 [82]	−0.112 [82]
I_2/I_3^-	0.36 [82] 0.71 [90]	0.86 [82,90]	0.396 [82] 0.65 [90]	0.27 [82]	0.344 [82]
I_2/I^-	0.31 [82,90]	0.36 [82,90]	0.26 [82,90]	—	0.273 [82,89]

The normal potentials (in V) are:

Medium	Neutral	Alkaline
I^-/IO^-	0.99 [82,85]; 1.313 [81]	0.49 [82,85]; 0485 [83]
I^-/IO_3^-	1.195 [84,85]; 1.085 [81,82]	0.26 [82—85]

In solutions containing chlorides $\phi^0_{I_2/ICl} = 1.19$ V [82,83,85] and $\phi^0_{I_2/ICl_2^-} = 1.06$ V [82,85] or 1.056 V.[83]

For the I_3^-/IO_3^- system $\phi^0 = 1.154$,[81] and for I_2/IO_3^- the following values of ϕ^0 have been reported:

t, °C	25	37.5	50
φ^0, V	1.1942 [91]; 1.195 [82,83]; 1.178 [81]	1.1903 [91]	1.1863 [91]

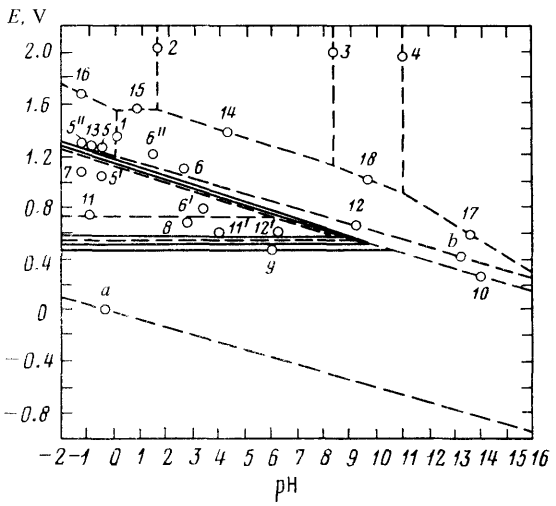


Figure 2. Potential–pH diagram for iodine[81] in the following systems: *a*) H_2/H^+, *b*) O_2/O_2^-, *1*) HIO_3/IO_3^-, *2*) HIO_4/IO_4^-, *3*) IO_4^-/HIO_5^{2-}, *4*) HIO_5^{2-}/IO_5^{3-}, *5*) I_2/HIO_3, *5'*) I_2/HIO_3 and I_2(s), *5''*) I_2(s)/HIO_3, *6*) I_2/IO_3^-, *6'*) I_2/IO_3^- and I_2(s), *6''*) I_2(s)/IO_3^-, *7*) I_2/I^+ and I_2(s), *8*) I^-/I_3^-, *9*) I^-/I_2, *10*) I^-/IO_3^-, *11*) I_3^-/I_2 and I_2(s), *11'*) I_3^-/I_2(s), *12*) I_3^-/IO_3^-, *12'*) I_3^-/IO_3^- and I_2(s), *13*) I^+/HIO_3 and I_2(s), *14*) IO_3^-/IO_4^-, *15*) IO_3^-/HIO_4, *16*) HIO_3/HIO_4, *17*) IO_3^-/IO_5^{3-}, *18*) IO_3^-/HIO_5^{2-}.

The pH dependence of the redox potential for various iodine compounds is shown in Fig.2.

III. REDOX PROCESSES IN I^-/I_2 AND I^-/I_3^- SYSTEMS

1. Electrolytic Oxidation of Iodide Ions

a) Studies by Faradaic impedance and rectification methods. The study of anodic and cathodic reaction kinetics in I_2/I^- and I_3^-/I^- systems is complicated by the strong diffusion control of the reactions[92]. Further difficulties arise from the adsorption of reactants and products in both anodic and cathodic reactions, and from the large number of independent paths available to the reactions.

Vetter[92] showed that the overall electrode reaction (2) takes place though the following steps:

$$I^- \rightarrow I\,(ads) + e \qquad (6)$$

$$2I\,(ads) \rightleftarrows I_2 \qquad (7)$$

$$I_2 + I^- \rightleftarrows I_3^-, \qquad (8)$$

reaction (6) being rate-determining. The kinetic order of the anodic reaction (p_a) with respect to I^- is 1, that of the cathodic reaction (p_c) with respect to I_2 is 1/2. This mechanism has been used[93,94] with a transfer coefficient $\alpha = 0.6$, but it was shown that at low concentrations of I^- the adsorption of I^- becomes rate-determining, and that electron transfer through a very thin adsorbed layer is slow.

Dane and coworkers[95] believe that Vetter's equations[92] are not generally applicable because they do not allow for changes in the coverage of the surface by I_2 and I^-, and they conclude that the impedance of the I_2/I^- system on a Pt electrode is unaffected by the adsorption of I^- and I_3^-, the rate-determining step being the Heyrovsky (electrochemical desorption) reaction

$$I^- + I\,(ads) \rightarrow I_2 + e\,. \qquad (9)$$

However, Tyagai's calculations[96] from Faradaic rectification data of the kinetic equations of the elementary steps [discharge–recombination, reactions (6) and (7), discharge–electrochemical desorption, reactions (6) and (9), and recombination–electrochemical desorption, reactions (7) and (9)], using the Langmuir, Temkin, and Frumkin adsorption isotherms, have clearly established that the electrode reaction mechanism for the Pt–I_3^-/I^- system consists of a series of discharge–recombination reactions with a slow discharge step, corresponding to the Langmuir isotherm.

The effect of surface non-uniformity on the kinetics of the electrode processes was studied by measuring the Faradaic impedance of an iridium electrode in the iodine–iodide system[97]. The electrode reaction on iridium was shown to take place only on active surface sites, whose size is smaller than the thickness of the diffusion layer. The extent of blocking of the Ir electrode increases with temperature.

b) Studies by voltammetry and oscillographic polarography. The anodic current–voltage curves for the oxidation of I^- in 3 and 6 M solutions of H_2SO_4 show one wave corresponding to the reversible oxidation [reaction (1)] of iodide to iodine[98]. In every case, irrespective of the composition and pH of the supporting electrolyte, this process begins at a potential of 0.55 V. A decrease in the anodic oxidation current of I^- has been observed[99] at 0.68–0.70 V (against the NHE). Changes in pH from approximately 0 to 12 have no effect on the potential at which the fall in current begins. This effect must be due to a retardation of reaction (2) [99] or (especially at the higher potentials, 1.6–1.7 V) to an oxide covering of the platinum surface[98].

The oscillographic polarograms for the oxidation of I^- obtained at 51 °C with a potential sweep rate of $\nu = 0.09$ V s^{-1} show a steep current rise followed by a fall[100], preceded by another clearly visible portion which becomes longer at high temperatures and disappears at low temperatures (20 °C). This additional feature of the polarogram is explained[100] by the evolution of liquid iodine on the electrode: the subsequent freezing of the iodine is responsible for the fall in current. The surface layer of iodine consists[101] of a dense part (next to the electrode) and a porous outer layer, and partial dissolution of the outer layer occurs while the dense inner layer becomes thicker. The decrease in current is due simply to the high resistance of the anodic film of iodine (0.18×10^5–7.0×10^5 Ohm cm).

A combination of oscillographic polarography and measurements of light intensity against time (ρ–τ) led to the conclusion[102] that the deposition of liquid iodine on the anode causes ρ to decrease, and the subsequent freezing of the layer results in a further increase in ρ. The maximum, and the final decrease in ρ, are ascribed to the consolidation of the iodine film.

In aqueous solutions reaction (1) is reversible on a Pt electrode[63,103], and in $HClO_4$ reaction (2) also takes place[103], the potential of reaction (1) being more positive than that of reaction (2). The second wave could correspond to the formation of I^+ [103,104] or of an oxide film[105,106].

The I^- ion has been studied by voltammetry also in other solvents; acetic acid[107–110], acetonitrile[90,111–117], DMF,[117–119], DMSO,[120] fluorosulphuric acid[121], nitromethane[90,122], pyridine[104,123,124], methanol[119,125], propanol[126], ethylene carbonate[127], propene carbonate[128], sulpholane[129], and acetone[90,113].

Changing from water to an organic solvent does not significantly alter the mechanism of the reactions in the I_2/I^- system: the oxidation of I^- in different solvents may involve either one or two steps. As Krishtalik points out[130], a change in the solvation energy of the electrically active ion is not directly reflected by the overvoltage of the electrode reaction. The indirect effect may be quite large, and lead to an increase in the concentration of non-solvated ions and in the stability of the I_3^- complex ion in different (protonic, or aprotic) solvents. The following values have been reported for the constant of the equilibrium (8): in water 10^3,[92,113] in t-butanol $10^{3.73}$,[131] in methanol $10^{4.2}$ (or $10^{4.94}$),[125,129,131] in isopropanol $10^{4.36}$,[131] in DMSO $10^{4.9}$,[131] in acetic acid $10^{5.0}$ (or $10^{5.24}$),[107,132] in acetonitrile $10^{6.6}$ (or $10^{6.75}$, $10^{4.0}$),[90,111,113,131] in nitromethane $10^{6.7}$,[90] in DMF $10^{7.35}$,[133] in sulpholane $10^{7.4}$,[129] and in acetone $10^{8.3}$.[90]

One-step oxidation of I^- is observed mainly in protonic solvents (water, methanol, acetic acid, etc.), the rate of the anodic reaction decreasing steeply (almost two-fold) from water to methanol and only slightly from methanol to CH_3COOH while the activation energy remains almost unaffected[119]. In aprotic solvents (acetonitrile, DMF, DMSO, nitromethane, etc.) the oxidation takes place in two steps: in the first the I_3^- complex is formed by reaction (2), and in the second it is discharged by the reaction

$$2I_3^- - 2e \rightarrow 3I_2 , \qquad (10)$$

because of the greater stability of I_3^- in these solvents.

In dilute (up to 10^{-3} M) methanolic solutions the I^- ion shows only one oxidation wave[125] to I_2 by Eqn.(1), whereas in more concentrated solutions the oxidation occurs in two steps through the formation of I_3^-. In acid methanolic solutions (pH 4.0) only one wave is observed [Eqn.(1)]. In weakly alkaline solutions (pH 8.5) two waves of approximately equal height are observed:

$$I_2 - 2e \rightarrow 2I^+ .$$

The I_2/I^- system in acetonitrile has been studied on pyrolytic graphite[112] by non-stationary and cyclic voltammetry, and three oxidation waves of I^- have been detected. The first has been assigned[113,114] to the irreversible reaction (2). The second wave is assigned to reaction (10), which is reversible according to the cyclic voltammetry method[112,127]. When an excess of iodine is added to a solution of KI in acetonitrile the I^- is converted into I_3^-, and the polarisation curve shows only the second wave with a height equal to the sum of the heights of the two I^- oxidation waves obtained in the absence of I_2.[114] Cyclic voltammetry has shown that the height of the cathodic peak is double the height of the anodic peak: this is explained[112] by the substantial adsorption of the electrically active I_2 species on the surface, as pointed out in Refs.63 and 65. The second wave shows a well developed anodic peak and a relatively small cathodic peak at low sweep rates (v) of the potential. This is explained by the instability of the product corresponding to the second peak. The cyclic voltammetry plots for the third wave do not show a cathodic wave in neutral or acid media[112]. Oxidation of I^- by reactions (2) and (10) is reported also in Ref.129.

In acidified pyridine four stable forms have been identified[124]: I^-, I_2, I_2^-, and I^+. The concentration of pyridine (even above 3 M) has no effect on the height of the first or the second wave in aqueous solutions, though the half-wave potential of the second wave is shifted towards more negative values[113]. The current decreases in the sequence pyridine > 2-picoline ≫ 2,6-lutidine (dimethylpyridine), which is the same as the order of decreasing basicity of these molecules.

At low concentrations of I^- (0.06 g-ion litre^{-1}) and especially in the presence of H_2SO_4 the potentiodynamic current–voltage curves[134] show two Tefel regions, corresponding to reactions (2) and (1), with the limiting current associated with the first step and the current peak with the second. The linear portions of the ϕ,lg i curves for the first step are parallel for different concentrations of KI, giving the order of the anodic reaction as $p_a = 2$.

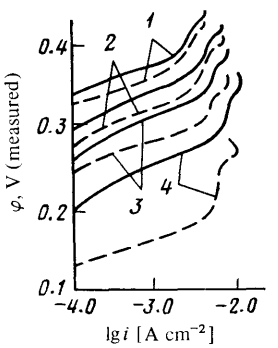


Figure 3. Anodic potentiodynamic curves in a solution (c_{KI} = 0.09 mole litre^{-1}) containing sulphuric acid (pH 0.62) in the presence (broken lines) and in the absence (full lines) of naphthenic acids for different potential sweep rates[136]: *1*) 0.04, *2*) 0.2, *3*) 0.4, *4*) 1.0 V min^{-1}.

The slope of the ϕ,lg i straight lines for the first step varies with the supporting electrolyte: in a solution without supporting electrolyte the slope is 0.042 V (α = 0.7), whereas in 1 *N* Na_2SO_4 it is 0.034 V (α = 0.87).[135,136] In the presence of an excess of supporting electrolyte the hydration of the I^- ions is suppressed, and this facilitates the discharge. Thus, in the presence of 1 *N* Na_2SO_4 the temperature coefficient of the overvoltage $(d\eta/dT)_i$ decreases from 3.5×10^{-3} to 0.85×10^{-3} V K^{-1}. Also, the activation energy of the process in 1 *N* Na_2SO_4 is much lower than in the absence of supporting electrolyte[135]. Even naphthenic acids (usually thought to be surface-active) lower the overvoltage for the oxidation of I^- (Fig.3), and when both the naphthenic acids and 1 *N* Na_2SO_4 are present together in solution the oxidation of iodide on platinum becomes almost barrierless (α = 0.97).[136] However, on a graphite electrode[137], and especially on a lead dioxide anode[138], the oxidation of I^- is strongly suppressed by naphthenic acids (Fig.4).

c) Studies by the rotating disk electrode method. The rates of the anodic and of the cathodic process are differently affected by the speed of rotation of a disk electrode ω:[139] a) the i,ϕ curves for the anodic and the cathodic process are asymmetric for different values of ω: b) the anodic reaction is ~10 times faster than the cathodic reaction; c) the rates of both processes are strongly influenced by stirring, but the effect is even more marked on the cathodic than on the anodic process.

At polarisation potentials <30 mV the rate of the anodic process is almost independent of ω, but for $\phi > 30$ mV the rate initially increases very rapidly with $\omega^{1/2}$ and reaches a constant level[140] for $\omega^{1/2} = 115-130$ min$^{-1/2}$. For fixed values of the potential and of ν the current increases with ω: the fall in current becomes sharp, and a large number of crystallisation centres appears on the electrode[141]. In a more concentrated solution (0.5 *N* KI + 0.01 *N* I_2) with $\omega = 580$ min^{-1} the fall in current no longer occurs, suggesting[141] a passivating role for the iodine film in the electrode process.

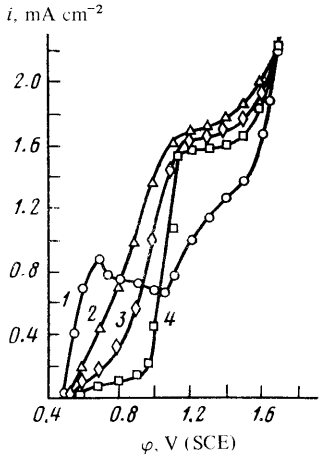


Figure 4. Anodic polarisation curves for the oxidation of iodide ions in an artificial concentrate on a lead dioxide electrode for different concentrations of naphthenic acids[138]: *1*) 0, *2*) 0.65, *3*) 1.02, *4*) 1.30 g litre^{-1}.

At low speeds of rotation of the electrode the overvoltage in the initial portion of the i, ϕ curve is close to that calculated by the Nernst equation (3).[97,142] However, as ω increases, the contribution to the polarisation from the slow electrochemical reaction also increases. Therefore in order to determine the kinetic currents (i_{kin}) for the oxidation of I^- we must extrapolate[142] the current at a given potential to an infinitely large value of ω by Frumkin and Tedoradze's method[143], since under these conditions linear (Tafel) regions are not found in the $\lg i-\phi$ curves. Extrapolation of the linear portions of the $\lg i_{kin}, \eta$ curves to $\eta = 0$ gave the exchange currents (i^0), which were shown[142] not to be equal for corresponding anodic and cathodic processes ($i_a^0 > i_c^0$, always).

The α_a and α_c values calculated from the slopes of the linear portions of the $\lg i_{kin}, \eta$ curves (i.e. the transfer coefficients for the anodic and the cathodic reaction) do not add up to 1. In solutions with $c_{I^-} \gg c_{I_2}$ we always find $\alpha_a + \alpha_c > 1$ (as high as 2 in some cases), whereas in solutions with similar concentrations of I^- and I_2 the sum is $\alpha_a + \alpha_c \leqslant 1$.[142] The order p_a is 1 with respect to I^- and 0 with respect to I_3^-. From these results it is concluded[142] that in the I^-/I_3^- system the overall electrode reaction (2) involves the two consecutive reactions (6) and (9), and the exchange current of the former reaction is greater than that of the latter.

The anodic oxidation of I^- becomes to a large extent irreversible when the solution pH is increased (pH > 1),[104] and it becomes reversible when the ratio $c_{I_3^-}/c_{I^-}$ decreases (with $c_{I^-} \leqslant 2.5 \times 10^{-4}$).[144] In very dilute solutions adequate kinetic currents are not obtained[145].

The order of the anodic reaction (1) with respect to I^- depends (though only slightly) on the supporting electrolyte present in solution[142]: without a supporting electrolyte $(\partial \lg i_{kin}/\partial \lg c_{I^-})_\phi = 1.3$, and in 1 *N* Na_2SO_4 $(\partial \lg i_{kin}/\partial \lg c_{I^-})_\phi = 1.0$. This effect is explained, according to Frumkin's theory[146], by the existence of a ψ' effect in the I_2/I^- system. Since in the presence of iodide ions the SO_4^{2-} ions are not specifically adsorbed, and the I^- ions irreversibly chemisorbed on Pt are not electrically active[63], we may assume[142] that the reacting species are mostly found on the outer Helmholtz plane of the diffusion layer, whose potential (ψ') varies with the concentration of the supporting electrolyte. Also, an increase in i^0 with concentration of the supporting electrolyte is possible only if ψ' is negative.

According to the present writer it is incorrect to ignore the decrease in hydration of I^- with increase in concentration of the supporting electrolyte. In the presence of electrolyte the concentration of non-hydrated I^- near the electrode surface increases, and this assists the discharge act. Hence in the presence of supporting electrolyte not only i^0 but also α should increase. In the absence of molecular iodine and under equilibrium conditions the inner Helmholtz plane consists of irreversibly adsorbed I^-(ads) species, and the outer plane of non-hydrated (or partially hydrated) I^- ions which are in equilibrium with the fully hydrated I' ions:

$$I^-(ads) \leftarrow I^- \rightleftarrows I' . \qquad (11)$$

When the oxidised form I_2 is also present in the solution (and adsorbed on the surface) the system becomes more complex:

$$\begin{array}{l} I^-(ads) \leftarrow \\ I_2(ads) \rightleftarrows I^- + I_2 \rightleftarrows I_3^- \rightleftarrows I' + I_2(aq) \rightleftarrows I_3' \end{array} \qquad (12)$$

Obviously the exchange current will increase with the concentration of I^- in both cases, but the dependence of the rate of the anodic process on $[I^-]$ will be more marked for (11) than for (12) because of the absence of I_3^- ions. Increasing the concentration of I_2 shifts the equilibria (12) towards the formation of I_3^-, which lowers the concentration of I_3^-, and should lower the limiting current of the anodic curve (as is found experimentally[139]). In the absence of the oxidsed form or with an excess of supporting electrolyte the equilibrium (11) is strongly displaced towards the left and the rate of the anodic process increases and becomes almost proportional to the square of the concentration of iodide ions[134,137].

It is interesting to consider whether adsorbed iodide can be oxidised. If a chemical compound of the MI_2 type is formed on the surface of the metal electrode this question cannot be answered meaningfully, but if physico-chemical adsorption (depending on the charge on the surface) is assumed, easy discharge of the adsorbed iodide can be expected.

After being immersed in a solution of KI for some time a platinum electrode gave a sharp current rise (at $\phi = 0.53$ V) followed by a slight fall. Even a second oxidation wave (iodine to iodate) has been observed at $\phi = 1.19$ V, and ascribed[148] to oxidation of adsorbed iodide. However, it is strongly argued[65] that oxidation of iodide does not take place on a Pt electrode previously immersed in an I^- solution: the adsorbed iodide is stated to be electrically inactive since the adsorption is irreversible and the exchange reaction $I^-(ads) \rightleftharpoons I^-(sol)$ is slow. These views are inconsistent with many published results[92,94,144,147]. It has been suggested[149] that the absence of an anodic oxidation wave for I^- on an electrode previously immersed in a solution of KI [65] could

be due to the influence of oxygen atoms resulting from the treatment of the platinum surface. Lukovtsev and coworkers[142,150,151] stress the lack of electrical activity of adsorbed iodine.

Various additives (ClO_4^-, CH_3COO^-, SO_4^{2-}, PO_4^{3-}, citrate ion) in I^- solutions lower the effective activation energy E_{eff} of the anodic process, the magnitude of the effect increasing with the concentration of the additive[152]. The dehydrating action of the added ions was suggested[152] as an explanation. At the higher additive concentrations the rate of the anodic process falls due to the adsorption of the added ions on the platinum surface[153]. Cationic additives (Hg_2^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}) lower the limiting current of both the anodic and the cathodic process[151] by being adsorbed on the electrode or by forming stable compounds with the iodide.

In DMF solutions the order of reaction (2) with respect to I^- is 1, and the adsorption of I^- on the electrode has been suggested[117] as the slow step of reaction (2), since DMF is adsorbed on platinum more strongly than water and thus inhibits the adsorption of I^-. The fall of the current in the i,η curves is also explained[117] by the slow desorption of iodine from the electrode surface rather than by the formation of a new phase (iodine film) postulated for water solutions.

As the concentration of DMF in a water + DMF mixture increases, the overvoltage of the anodic reaction increases gradually, reaching its highest value in pure DMF.[118] On the anodic curves for the oxidation of I^- in a medium containing relatively small additions of water to DMF (2.2 and 11 M H_2O in DMF) two I^- oxidation waves are observed, as in pure DMF.[117] As the water content of the mixed solvent is increased, the first wave becomes indistinct, and at the potentials of the second wave we observe a sharp rise in current with an associated fall, as in the case (water solution) of the formation of a surface film on the electrode[101,114]. When the concentration of DMF in the mixture is increased, i^0 decreases and the sum of α_a and α_c changes from 2 (in pure water) to 1 (in pure DMF). It has been suggested[118] that in DMF and its mixtures with water (as in pure water) the overall electrode reaction involves two consecutive steps: discharge and electrochemical desorption [reactions (6) and (9)], with comparable exchange currents. The same mechanism# is proposed for DMSO [120] and acetonitrile[111].

d) Studies by chronopotentiometry. The kinetics of electrode reactions in the I^-/I_2 system have been studied[64] by the application of very short galvanostatic pulses, assuming the mechanism of the anodic and the cathodic reaction proposed by Vetter[92].

The chronopotentiograms for the electrolytic oxidation of I^- in water, methanol, 1-butanol, 2-propanol, and acetic acid indicate the formation of I_2 by a single one-electron step[104,110]. Two-step oxidation of I^- to I_2 was observed[110] in ethylene glycol, acetonitrile, acetone, 1,2-dimethyloxyethane, nitromethane[154], DMSO, and acetic anhydride. In pyridine (Py) the anodic reactions $I^- \to I$ and $I \to I^+$ take place[110,113] in spite of the fact that I_3^- is more stable than PyI_2.[155] The addition of NaI to a solution of I_2 in pyridine produces three steps on the chronopotentiogram, with $E_{1/4}$ values of 0.35, 0.5, and 0.9 V respectively, corresponding to reactions (2) and (10), followed by the oxidation of I_2 to I^+ [110] as a result of the dissociation of the iodine molecule in pyridine[123]:

$$2I_2 + Py = PyI^+ + I_3^- .$$

In the presence of chloride ions the oxidation of I^- in nitromethane[154] takes place by the reaction

$$I^- + Cl^- - 2e \to ICl . \qquad (13)$$

2. Electrolytic Reduction of Iodine and of the Iodine–Iodide Complex

a) Studies by Faradaic impedance and rectification methods. Vetter's Faradaic impedance method[92] has established the value of p_c for the electrochemical reduction of iodine on platinum by the overall reaction

$$I_3^- + 2e \to 3I^- \qquad (14)$$

and has led to the following mechanism for the process:

$$I_3^- \to I_2 + I^- \qquad (15)$$

$$I_2 \to 2I \qquad (16)$$

$$I + e \to I^- , \qquad (17)$$

in which the discharge is the slow step. The same mechanism has been proposed[156] for the electrolytic reduction of I_3^- on a porous graphite electrode in acid or neutral protonic solvents, with the following kinetic parameters:

α_c	α_a	p_c (for I_3^-)	p_a	p_c (for I^-)	p_a
0.5	0.5	0.5	0	−0.5	1

Simultaneous measurements of the Faradaic impedance and of rectification[157] have confirmed the scheme involving reactions (16) and (17). The transfer coefficient of the discharge step is given[157] as 0.47 (±0.04), but other workers[144, 150,151] report an α value varying regularly with the concentration of iodine in solution. The rate constant of the cathodic reduction of I_3^- is $(1–5) \times 10^{-2}$ cm s^{-1},[157] and it is assumed that at low coverages by adsorbed iodine ($\theta \to 0$) $p_c(I_2) = p_c(I_3^-) = \alpha = 1$, and the cathodic reduction of iodine on CdS and CdSe electrodes takes place by the discharge–electrochemical adsorption mechanism[157]

$$I_2 + e = I^- + I\,(ads) , \qquad (18)$$

with simultaneous rate limitation by the two electrochemical steps.

b) Studies by voltammetry and oscillographic polarography. The shape of the cathodic wave on the voltammetric curves measured on a platinum electrode is independent of the direction of the potential sweep[104]. The diffusion current is proportional to the concentration of I_2, and the ratio i_d/c_{I_2} is 190 μA mM^{-1}. In the absence of Cl^- ions the iodine is reduced by the reaction

$$I_2(aq) + 2e \rightleftarrows 2I^- , \qquad (19)$$

but in 4 M HCl the iodine exists mainly as the iodine–chloride complex (I_2Cl^-), and the electrode process corresponds to the reaction

$$I_2Cl^- + 2e \to 2I^- + Cl^- . \qquad (20)$$

In 0.1 M perchloric acid and in the presence of 0.05 M sodium cyanide the cathodic iodine reduction wave is not observed. Iodine cyanide, formed by the reaction

$$HCN + I_2 \rightleftarrows H^+ + I^- + ICN , \qquad (21)$$

is not reduced on platinum, and no free iodine is present[104].

On a Pd electrode the reduction of iodine is irreversible up to an overvoltage of ~500 mV, beyond which a steep current rise is observed, associated[158] with the reduction of the

At high positive potentials and low surface coverages the rate-determining step of the second wave in DMSO is thought to be the reaction[120] $I_3^- + M \rightleftarrows M(I_3) + e$.

film of iodine on the electrode surface. When this film has been removed the electrolytic reduction of iodine becomes much faster, reaching the limit set by the diffusion current. The existence of a "pre-wave" on the polarisation curve for the electrolytic reduction of iodine on Pd is explained by the partial blocking of the electrode at η values up to 0.5 V, so that the observed limiting currents are lower than those for an electrode with a uniform surface.

Since I_3^- is much more stable in DMF than in aqueous solutions, the species which is reduced in DMF is not I_2 but I_3^-.[118] The potentiodynamic curve for the reduction of I_3^- in DMF includes a limiting current plateau followed (beginning at $\eta = 0.8$ V) by a decrease in current arising from the negative charge of the reacting species[159]. This explanation implies that in the presence of an excess of I_2 (and in contrast to the case of high concentrations of I^-) no current fall should occur at potentials up to −2.0 V. During the reduction of I_3^- the curves plotted in the reverse direction always lie below the forward plots. Furthermore, the depth of the current minimum (beyond the current fall) decreases as the potential sweep rate increases, and disappears completely at the highest rates ($v \geq 40$ mV s^{-1}). According to Povarov and coworkers[159], at potentials close to the equilibrium value I_2 is reduced to I_3^-:

$$3I_2 + 2e \rightarrow 2I_3^- , \qquad (22)$$

and in the presence of high concentrations of KI the iodine–iodide ion is further reduced to I^- by reaction (14). These processes take place through the adsorption of I_2 and I_3^- on the electrode. At sufficiently high negative potentials the iodine is desorbed from the surface, and subsequent reduction takes place without adsorption. "Stretched" irreversible waves are observed in the reduction of iodine, and inhibition of the reaction in the case of I_3^- reduction: thus the process appears to be determined by the rate of penetration of I_3^- into the EDL.

Two-step reduction of iodine by reactions (22) and (14) has been observed also in acetic anhydride[107].

c) Studies by the rotating disk electrode method. A diffusion-limited current is observed[104,144,151,160] in the reduction of I_3^- on a Pt electrode. Under both turbulent and laminar stirring regimes a well defined plateau is observed on the cathodic i,ϕ curves for a 0.1 M I_2 + 1 M KI solution at different values of ω, and the limiting diffusion current varies linearly[160] with $\omega^{1/2}$, the activation energy of the cathodic process under laminar stirring being almost one-half the value for turbulent stirring. The activation energy of the process (E_{eff}) is also a function of the rate of rotation of the electrode: at first E_{eff} increases with $\omega^{1/2}$, but at the higher values of ω (beyond $\omega^{1/2} = 110$ $s^{-1/2}$) E_{eff} becomes constant[139]. The rate of the cathodic process also increases in proportion to the concentration of I_2.[139]

These results confirm that the rate-limiting process (as in the anodic process) is the diffusion of the reacting ion towards the electrode. But since the products of the anodic and the cathodic process are removed from the electrode at different rates, i.e. fairly slowly in the case of the anodic process (iodine–iodide complex) and rapidly in the case of the cathodic process (iodide ion), the oxidation and the reduction processes in the I_2/I^- system are affected by ω to different extents. For $\omega = 3000$ min^{-1} the rate of the cathodic process increases by a factor of 22.4 (as compared to the rate for $\omega = 0$), whereas the rate of the anodic process increases only by 9.6.[139] However, in a solution containing ~10 times more I_2 than I^- the rate of the cathodic process is ~10 times higher than the rate of the anodic process[140]. At high speeds of rotation the parameter ω no longer affects the rate of cathodic reaction[139,140], indicating electrochemical rate control.

Because iodine is reduced with a high overvoltage on a rotating Pd electrode[158] the order p_c with respect to I_2 can be determined from the kinetic currents obtained by extrapolation of the $i^{-1}, \omega^{-1/2}$ curves to $\omega \rightarrow \infty$: for $\eta = 100$–150 mV, $p_c = 1$.[158] On a Pt electrode the p_c value for I^- and I_2 could not be determined accurately[142,158], because the slope of the linear portions of the $\lg i_{kin} - \phi$ curves varies with the concentration of I^- and I_2. By using curves with similar slopes the parameter p_c was determined approximately for I^- and I_2: $p_c(I_2) = 1$ and $p_c(I^-) = -1$.[142] The negative order of p_c with respect to iodide suggests[142] that the kinetic unit in the cathodic process is I_2 rather than I_3^-. Thus, as the potential of the electrode is made more negative the bond between I^- and I_2 in the I_3^- complex should be weakened by the repulsion forces acting on the iodide, which favour the formation of adsorbed atoms or molecules of iodine on the electrode surface[64].

From the initial portions of the i,ϕ curves obtained in a study[144] of the electrolytic reduction of iodine on a rotating Pt electrode, which gave the kinetic parameters of the cathodic reaction, the order p_c was found to depend both on the concentrations of I_2 and I^- and on ω. This result was explained[144] in terms of the non-uniformity of the electrode surface. It was shown that electron transfer from the platinum to an adsorbed iodine atom is the slow step in this case. The height of the cathodic I_2 reduction waves on Pt is unaffected (within experimental error) by changes in the acidity of the solution[98], but the limiting current decreases if the time of immersion of the electrode in the solution is increased[151]. These changes in current on an activated electrode can be as high as 20–30% of the i_d value for the first wave in a solution containing an excess of supporting electrolyte (Na_2SO_4). In solutions containing only I_2 and I^- the time dependence of i_d is slighter, and decreases with the concentration of iodine. The changes in limiting current are ascribed[151] to non-uniformity of the platinum surface, produced by the irreversible adsorption of iodine on Pt.

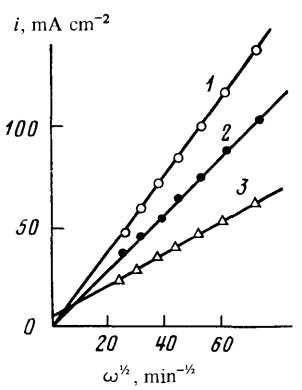


Figure 5. Cathodic limiting current against speed of rotation of the platinum electrode for a 0.2 M KI + 2×10^{-2} M I_2 solution at different temperatures[150]: *1*) 50, *2*) 25, *3*) 1 °C.

The surface non-uniformity of the platinum[139] and of the iridium electrode[97] causes anomalous variations of i_d with $\omega^{1/2}$: at low temperatures (1 °C) the extrapolation of the linear $i_d, \omega^{1/2}$ plots for the reduction of iodine does not pass

through the origin[150] (see Fig.5). A quantitative interpretation of this observation was proposed[150] by introducing into the Levich equation an additional term as required by Landsberg's theory[161], independent of ω and determined by the number of active sites on the electrode surface and on the distance between these sites:

$$1/i_d = 1.61\nu^{1/6}/nFD^{2/3}c\omega^{1/2} + \left|\sum A_n\right|/nFDc\,, \qquad (23)$$

where $|\Sigma A_n|$ is the non-uniformity function of the electrode surface, which increases with the non-uniformity, i.e. as the ratio of the radius (r_1) to the spacing (r_2) of the active sites decreases.

According to Landsberg[161] if $r_2 > \delta$ (where δ is the thickness of the diffusion layer) the current i_d is given by the equation

$$i_d = nFD^{2/3}\omega^{1/2}/1.61\nu^{1/6}\left(1 + \left|\sum A_n\right| r_n/r_2\right)\,, \qquad (24)$$

and if $r_2 \ll \delta$, i_d is given by Eqn.(23). It is pointed out[151] that at ordinary temperatures $r_2 > \delta$ on a platinum surface, and therefore i_d is given by Eqn.(24). At lower temperatures the size of the active sites decreases and we have $r_2 < \delta$, leading to a non-linear dependence of i_d on $\omega^{1/2}$ [Eqn.(23)]: a possible explanation of the decrease in radius of the active sites at low temperatures is the chemisorption of ions on the electrode surface[150]. The surface of the iridium electrode in the I_2/I^- system is partially blocked, and the active sites are small. Therefore the variation of i_d with $\omega^{1/2}$ is as predicted by Eqn.(23).[97] The surface of the palladium electrode is fairly uniform: a large number of small active sites is present on an active palladium surface. However, the number of active sites decreases with time, and the Pd electrode becomes similar to the iridium electrode, with relatively few, small active sites, so that for a partially poisoned Pd electrode we can write $r_2 \ll \delta$. When the electrode surface is uniform the E_{eff} value for the limiting diffusion current is determined by the activation energy for viscous flow, as in the case of the Pt electrode§. However, for the Ir electrode[97] the activation energy is lower, and it is a function of ω. The activity of the iridium surface decreases as the temperature rises: this effect is partially compensated by the increased rate of diffusion.

When zinc and mercury ions are present in solution the time dependence of i_d is even more marked[151]. At sufficiently negative potentials the surface is blocked by a film of zinc iodide, which causes a sharp fall in current, and the electrolytic reduction of I_2 and electrodeposition of zinc are suppressed. Mercury ions are adsorbed with the iodine, lowering the rate of both the anodic and the cathodic reaction. Zinc ions also increase the amount of iodine irreversibly adsorbed on the electrode surface, but the effect is less marked than with mercury. Cadmium ions have a smaller effect than Zn^{2+} ions on the cathodic reduction of iodine. They are adsorbed on Pt over a wide range of potential[162], and their effect on the cathodic process is negligibly small, but they lower the rate of the anodic process. A possible explanation[162] is the suppression of iodine adsorption, and hence of the rate of the electrochemical desorption (9), by the adsorbed Cd^{2+} ions. The adsorption of Cu^{2+} on Pt prevents the formation of Pt–I^- bonds but it has almost no effect on the amount of iodine reversibly adsorbed on the electrode surface[151]. Unlike mercury ions, which block the surface by forming iodine compounds, metallic mercury deposited on a Pt surface has very little effect on the current[151]. The presence of Cl^- ions does not affect the half-wave potential for the reduction of I_2 to I^-, or the reversibility of the process[164].

The fluctuation of the limiting reduction current of I_2 is also ascribed to surface non-uniformity[165]. On a platinised platinum electrode the mean amplitude of the oscillations of the limiting current is lower by almost a factor of two than on smooth platinum, and decreases faster than on smooth platinum with increase of ω.[165] Potential and current oscillations have been observed[84] in the I_2/I^- system, and ascribed to turbulence in the flow of electrolyte. The adsorption of Hg^{2+} on the electrode surface minimises the fluctuations in the limiting current[165], and the adsorption of DMF suppresses them completely. DMF solutions (unlike water solutions) show a fall in current (after the limiting current) accompanied by much stronger fluctuations[159].

In DMF two limiting currents for the cathodic reduction of iodine are observed, and both are free from oscillations. These waves correspond to reactions (22) and (19).[117]

Since the slopes of the $\Delta\phi$, $\lg(1 - i/i_d)$ plots for both these waves are substantially higher than their theoretical values the authors[159] conclude that the processes are irreversible, especially in the case of reaction (19), due to the absence of adsorbed iodine. When an excess of I^- is present in solution the cathodic curve consists of one wave, and the reaction is

$$I_2\ (ads) + I^- \rightleftarrows I_3^-. \qquad (25)$$

In solutions containing more I_2 than I^- the reduction of I_2 is kinetically of the first order, and the most likely slow step is the adsorption of iodine on the electrode surface[159]. In ethylene glycol[166] and acetonitrile[111] with $[I_2] > [I^-]$, I_2 and I_3^- are reduced successively by reactions (22) and (14). In acetonitrile both the first and the second cathodic process go through the rate-determining step (18).[111] In DMSO [120] the rate-determining step is the reaction

$$I_3^- + e \rightarrow I\ (ads) + 2I^-. \qquad (26)$$

In methanolic solutions[119] the iodine is reduced as in aqueous solutions, with more marked stirring effects on the cathodic than on the anodic process.

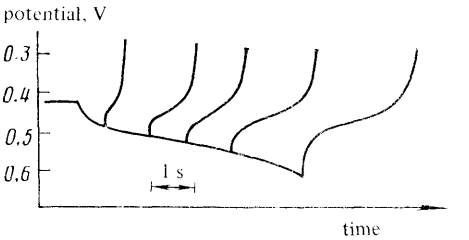


Figure 6. Effect of applying reverse current at various points of the chronopotentiogram for the oxidation of iodide ions[65].

d) Chronopotentiometric studies of the reduction of iodine in DMSO have given results consistent with those of the rotating disk electrode method: in particular, reaction (14) was shown to be irreversible. However, its rate constant determined chronopotentiometrically [$(1.12–2.86) \times 10^{-4}$ cm

§ An activation energy of 2.2 ± 0.1 kcal mole^{-1}, independent of ω, was obtained[97] from the slope of the $\lg i_d, T^{-1}$ straight lines. This is consistent with the published values[160,163] 2.08 and 1.88 kcal mole^{-1} respectively.

s^{-1}] is lower than the value obtained on a rotating disk electrode (6.8×10^{-4} cm s^{-1}).[120]

Contradictory conclusions as to the lack of electrical activity of adsorbed iodine have been drawn from chronopotentiograms. According to Hubbard and coworkers[63] only reversibly adsorbed iodine can be reduced cathodically, and the amount of electrically active iodine on the Pt surface is much less than the strongly bound iodine. However, Osteryoung and Anson[65] find that the reverse (cathodic) chronopotentiograms taken at different points of the anodic chronopotentiogram give transition times proportional to the amount of iodine evolved anodically and adsorbed on the electrode surface (Fig.6). According to Schuldiner and Presbrey[64] even α_c depends on the number of iodine atoms adsorbed on the Pt. The high rate of oxidation of I_2 chemisorbed on PbO_2 has been pointed out[62].

IV. REDOX REACTIONS IN I^-/IO_3^-, I_2/IO_3^-, AND I_2/I^+ SYSTEMS

1. Anodic Processes

Unlike the electrolytic oxidation of iodide to iodine, the deep oxidation of I^- to oxygenated compounds, in particular by the reaction

$$I^- + 3H_2O - 6e = IO_3^- + 6H^+, \quad (27)$$

depends on the pH of the electrolyte, as has been confirmed experimentally. Changing the pH between 5.85 and 1.72 produced a linear shift in potential towards more positive values[98] by 0.06 V for each pH unit, as required by Eqn.(27). Further increase in acidity did not affect the potential.

Since the "reverse" voltammetry curves (i.e. those plotted by decreasing the positive potential after the anodic wave corresponding to the formation of IO_3^-) do not reproduce the wave given by the oxidation of iodide to iodate[98,104], a mechanism involving the participation of oxygen from surface oxide layers of the platinum has been suggested[98]:

$$PtO[O]_n + I^- \rightarrow IO_3^- + PtO[O]_{n-3}. \quad (28)$$

The current fall observed on the polarisation curves is also ascribed to the formation of surface oxide layers on the platinum. It is suggested that reaction (27) takes place at 0.9–1.2 V, whereas at more positive potentials the oxidation of I^- involves the scheme (28). It has been established[148] that the second anodic oxidation wave of I^- corresponds to the deep oxidation of iodine:

$$I_2 + 6H_2O - 10e \rightarrow 2IO_3^- + 12H^+. \quad (29)$$

On an electrode consisting of a mixture of graphite and azobenzene[167] and on a pyrolytic graphite electrode[112,168] two iodide oxidation waves have been observed: to hypoiodite and to iodate. The height of these waves is proportional to the concentrations of I^- and I_2, and depends on ω. The total height of the waves is determined by the diffusion of OH^- to the electrode (for intermediate concentrations of OH^-). The electron transfer reaction for the iodate formation step is of the first order with respect to I^-; with respect to OH^- the order is 0.23 at pH 6–10.6 and zero at higher pH values. hence we may conclude that in alkaline solutions I^- is discharged on the surface sites where OH^- ions are adsorbed[167]:

$$I^- + OH^- \rightarrow HIO + 2e \quad (30)$$

$$I^- + 6OH^- \rightarrow IO_3^- + 3H_2O + 6e \quad (31)$$

or

$$M + OH^- \rightarrow M{-}OH + e \quad (31a)$$

$$x(M{-}OH) \rightarrow M{-}(O)_x + xH_2O \quad (31b)$$

$$M{-}(O)_x + I^- \rightarrow M{-}(O)_{x-3} + IO_3^-. \quad (31c)$$

In solutions of pH > 6.5–7 free iodine cannot take part in the anodic reaction because of its disproportionation

$$I_2 + OH^- \rightleftarrows IO^- + I^- + H^+ \quad (32)$$

$$3I_2 + 3OH^- \rightleftarrows IO_3^- + 5I^- + 3H^+. \quad (33)$$

In iodic acid solutions the $\lg i, \phi$ curve for Pt, Pb, and PbO_2 electrodes[169] has two linear portions, corresponding to two controlling steps for the oxidation of iodine to highly oxygenated compounds by the reactions (29) and (34):

$$HIO_3 + H_2O - 2e = HIO_4 + 2H^+, \quad (34)$$

the rate of the latter reaction determining the rate of the overall process. On a PbO_2 electrode (or on anodically oxidised lead) the iodine is oxidised by the oxidation products of water, and in particular by $OH^\cdot$ radicals according to the mechanism (31a)–(31c).

It has been shown[104] that in acid aqueous solutions of I^- two anodic waves [corresponding to reactions (1) and (35)] are obtained:

$$I_2 - 2e \rightarrow 2I^+. \quad (35)$$

The maximum current of the second wave is equal to twice the diffusion current of the first wave. At pH 8 the two waves merge, but the limiting current still corresponds to the quantitative oxidation of I^- to I^+. In a medium containing 0.05 M NaCN and 0.1 M $HClO_4$ the I^- ion gives an anodic wave with a height double that for an iodine solution of the same normality:

$$I^- + HCN \rightarrow ICN + H^+ + 2e. \quad (36)$$

These results[104] are not confirmed by chronopotentiometric data[170–172], which suggest that the second anodic wave in the oxidation of I^- is associated with reaction (29) rather than with the formation of I^+ by reaction (35), since this wave is completely suppressed when the electrode is polarised from an oxidation towards a reduction potential.

Measurements by the rotating disk electrode method with a guard ring have shown[164] that positively charged iodine ions (I^{n+}) are formed by the deep oxidation of I^- on a disk electrode and are transferred by convective diffusion to the ring electrode where they react with the I^- in solution as follows:

$$I^{n+} + nI^- = 1/2(n+1)I_2. \quad (37)$$

This explains the failure of positively charged forms of iodine to give a reverse electrolytic reduction wave. A mechanism involving reaction (27) was assumed[164], as in Ref.170, on the grounds that the ratio of the limiting currents for the first and the second I^- oxidation wave is six. However, it should be noted that the participation of the Cl^- ions in the electrode process was ignored in that work[170], though these ions are known to affect the mechanism of the deep oxidation of I^-. In the presence of a high enough concentration of Cl^- the first anodic wave corresponds to the oxidation of iodide to iodine [reaction (1)] followed by the formation of the iodine–chloride complex, and the second wave to the conversion of I_2Cl^- into iodine chloride[104,164,173–176]:

$$I_2Cl^- + 3Cl^- \rightarrow 2ICl_2^- + 2e. \quad (38)$$

The charge transfer processes in reactions (13) and (38) are polarographically reversible on smooth platinum[177].

In chloride solutions the I_2Cl^-, ICl, ICl_2^-, and I_3^- complexes are stable, with $[I_2Cl^-]/[ICl]\cdot[I^-] > [I_2Cl^-]/[I_2]\cdot[Cl^-] > [I_3^-]/[I_2]\cdot[I^-] > [ICl_2^-]/[ICl]\cdot[Cl^-]$.[177,178]

In methanolic solutions[125] and in acetic anhydride[107] iodine is oxidised to I^+, but the half-wave potentials for the oxidation of I_2 to I^+ and for the reduction of I^+ to I_2 are not the same at a given pH. In methanolic solutions the redox couple is thought[125] to be not I_2/I^+ but the iodine–iodonium methoxide couple:

$$I_2+2CH_3OH\rightarrow 2CH_3OI+2H^++2e\ . \qquad (39)$$

Iodonium methoxide is unstable and decomposes into iodates. The insolubility of iodates in methanol and the growth of an iodate layer cause passivation of the electrode.

In acetic anhydride[107] the iodine is initially oxidised to I^+, and then the I^+ reacts further with the acetic acid

$$I_2+2CH_3COOH-2e\rightarrow 2CH_2ICOOH+2H^+ \qquad (40)$$

to give monoiodoacetic acid which is decomposed in the next step by the Kolbe reaction

$$CH_2ICOOH-e\rightarrow (CH_2I)^\cdot+CO_2+H^+ \qquad (41a)$$

$$(CH_2I)^\cdot+H^+\rightarrow (CH_3)^\cdot+I^+\ . \qquad (41b)$$

2. Cathodic Processes

Iodine monochloride gives two scarcely distinguishable electrolytic reduction waves[104,179]:

$$2ICl_2^-+2e\rightarrow I_2Cl^-+3Cl^- \qquad (42)$$

$$I_2Cl^-+2e\rightarrow 2I^-+Cl^-\ . \qquad (43)$$

The reduction of ICl to I_2 is reversible, whereas the reduction to I^- is reversible only for $c_{H^+} < 0.3$ M.[164] The reversibility of the reduction of ICl_2^- to I_2 is influenced both by the concentration of HCl and by the state of the electrode surface. On smooth platinum the reduction of ICl_2^- to I_2Cl^- is quasi-reversible for $c_{HCl} \leq 1$ M, and becomes fully reversible for $c_{HCl} = 4$ M.[82]

On the dropping mercury electrode the reduction potential of IO_3^- in alkaline solutions is independent of pH, but in acid solutions it becomes less negative as the pH decreases[82].

The electrolytic reduction of iodates in aqueous, ethylene glycol, and propylene glycol solutions is essentially a catalytic reaction, different organic or inorganic additives affecting its rate in different ways[180]. Increasing the concentration of $NaClO_4$ lowers the reduction potential of IO_3^-; additions of $N(C_4H_9)_4^+$ in small amounts increase the rate of reduction, but in large amounts they inhibit the reduction by being adsorbed on the electrode. It is clear from the polarograms for the electrolytic reduction of IO_3^- [181] that gelatin, tylose, X-100 Triton, cetylpyridinium bromide, and cetyltrimethylammonium bromide behave as inhibitors towards this process, whereas *N,N*-dimethyl-*p*-phenylenediamine, hexamine, hydrazine, and polyethyleneimine catalyse it. It is suggested[181] that in acid and in neutral solutions the rate-determining step is a one-electron process, and in alkaline solutions a two-electron process, the slow step being the transfer of the second electron (involving breaking of the first bond between iodine and oxygen atoms).

Chronopotentiometric curves have been used[182] to determine the kinetic parameters of the reduction of IO_3^-. From the slope of the plot of ϕ against $\lg[1-(t/\tau)^{1/2}]$, where τ is the transition time, the authors[182] calculated the change in valency of the I during the slow step (unity), the coefficient $\alpha = 0.5$, and the order $p_C = 0.5$ with respect to iodates. However, according to Vetter[84] $\alpha = 0.6$ and is independent of the concentrations of IO_3^- and I^-, and the rate of the transition is proportional to the square root of the concentration of H^+ ions.

The reduction of iodate ions on platinum is strongly influenced by the state of the platinum surface. The reduction of IO_3^- is found[183] to be more reversible on the oxidised than on a reduced platinum electrode. The positive shift (by ~0.4 V) of the IO_3^- reduction potential caused by oxidising the electrode is explained[183] by postulating a catalytic interaction between the oxide films on the platinum surface and the iodate reduction process. However, the mechanism of the catalytic effect of the oxide films is not stated, though it is pointed out that the reduction of the oxide films begins before the reduction of IO_3^-.[183] The suggestion (from chronopotentiometric data) that oxide films may play a catalytic role is confirmed by voltammetry results: an additional peak at ~0.3 V in the i,ϕ curves for an oxidised platinum electrode, not observed for any other state of the electrode[183].

A mechanism for the electrolytic reduction of IO_3^- which allows for the postulated catalytic effect of oxide films has been proposed[184]. The role of the platinum oxides is interpreted as an increase in the rate constants of the dissociative chemisorption equilibria:

$$IO_2OH\rightleftarrows IO_2^+(\text{chem})+OH^-(\text{chem}) \qquad (44)$$

$$IO_2^+(\text{chem})+H_2O\rightleftarrows IO_2^++H^++OH^-\ . \qquad (45)$$

These catalytic changes produce substances which can be reduced at a lower overvoltage than the starting material.

The cathodic process in an IO_3^- solution in 0.1 M H_2SO_4 is catalysed also by sulphur atoms electrochemically adsorbed on the platinum surface from a solution of H_2S in 0.1 M H_2SO_4 or of 0.1 M Na_2S.[185] By comparing the polarisation curves for electrodes with and without a sulphur coating, and also for electrodes covered with oxygen, we can show that in the first case the half-wave potential ($E_{1/2}$) for IO_3^- is more positive than in the second case, but more negative than in the third. Hence the activating influence of sulphur is less effective than that of oxygen. The activation of the cathodic process by sulphur atoms has been explained[185] by an increased coverage of the electrode surface by IO_3^- ions in the sulphur-covered areas, due to the formation of stable compounds between IO_3^- and the adsorbed sulphur.

Vetter[84] noted a strong increase in the limiting current for the reduction of iodates at high concentrations of I_2. He ascribed the acceleration of the cathodic process by the addition of I_2 or by a decrease in pH to a fast ($E_{eff} = 5$–10 kcal mole^{-1} [186,187]) chemical reaction between IO_3^-, H^+, and I^- (the latter being formed by the direct reduction of IO_3^- or I_2):

$$IO_3^-+6H^++6e\rightarrow I^-+3H_2O\ (\text{slow}) \qquad (46)$$

$$5I^-+IO_3^-+6H^+\rightarrow 3I_2+3H_2O\ (\text{fast}). \qquad (47)$$

Anson[183] rejected Vetter's conclusion[84] and showed that the reduction of IO_3^- is independent of pH in the pH range 1–6, even with allowance for the formation[188] of iodine as an intermediate in the reduction of IO_3^- by a mechanism which includes reactions (46) and (47).

In the polarisation curves measured on a rotating disk electrode the autocatalytic mechanism including reactions (46) and (47) is more important at low rotation speeds ($\omega < 1600$ min^{-1}) than at high speeds[179]. The catalytic reduction is accelerated by increasing the concentration of IO_3^-.[164] The more positive half-wave potential for the reverse plot (i.e. for a potential sweep from the negative towards the positive values) than for the normal plot (Fig. 7) is also explained by the autocatalytic reduction of IO_3^-.[164] The observation that the direct reduction of iodate [reaction (46)] on a smooth platinum electrode in a 1–5 M H_2SO_4 supporting electrolyte requires a high overvoltage has led to the same conclusion[189].

In a hydrochloric acid medium at concentrations up to 3 M the cathodic processes include reaction (46) as the rate-determining step and the following fast reactions:

$$2I^- + IO^-_3 + 3Cl^- + 6H^+ \rightarrow 3ICl + 3H_2O \quad (48)$$

$$ICl + 2e \rightarrow I^- + Cl^- . \quad (49)$$

The electrochemical product I^+ is formed in substantial amounts when the concentration of I_2 is much greater than that of I^-.[164]

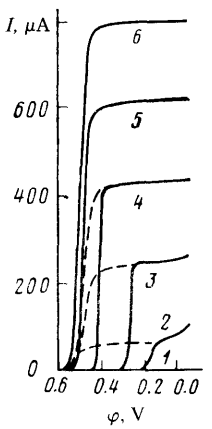


Figure 7. Reduction of IO_3^- in an HCl solution (rotating platinum disk electrode, $A = 0.36$ cm^2, $\omega = 400$ min^{-1}, $\nu = 0.4$ min^{-1}). Full lines denote potential sweep from (+) to (−), broken lines from (−) to (+):[164] *1*) 0.2 M HCl + 0.3 M NaCl, *2*)–*6*) with added KIO [10^4 c_{KIO}, mole litre^{-1}: *2*) 2 *3*) 4, *4*) 6, *5*) 8, *6*) 10].

In an acid 0.1 M phthalate buffer (0.01 M IO_3^- + 0.1 M KCl at pH 3.2) the catalytic effect is observed, and the current density and the kinetic parameters of the process vary with time[188]. Moderately fast stirring lowers the current at a given potential by the partial removal of iodine. In an alkaline 0.05 M borate buffer (0.01 M IO_3^- + 0.1 M KCl at pH 9.2) the current density is effectively independent of time. However, in the presence of camphor changes with time are observed. If KI is added to the borate buffer to a concentration of 0.1 M the current density changes with time both in the absence and in the presence of camphor. According to Vetter[84] a different mechanism should apply in an alkaline solution in which the iodine disproportionates according to reaction (33).

Thus we can infer from the inconsistency of published results on the mechanism and kinetics of the oxidation of I^- that the electrode processes in the I^-/I_2 system are so dominated by diffusion-limited kinetics that $i_0(6)$ and $i_0(9)$ are almost impossible to measure by any of the standard methods. Depending on the state of the I^- in the outer Helmholtz plane, and on the appearance of a ψ^- potential (which is often observed, especially in the presence of a supporting electrolyte, since I^- has "negative hydration"[190]), the rates of transfer of the first and the second electron in the overall reactions (1) and (2) can be very similar. The oxidation of I^- to I^{n+} is also very important; the reduction of IO_3^- to I^- is autocatalytic, but this mechanism has not been observed in the oxidation of I^- to IO_3^- (though it has been observed, at least in part[175], during the formation of ICl in the presence of Cl^-).

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Mechanism of the Epoxidation of Alkenes by Molecular Oxygen

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Radical and molecular mechanisms of the formation of oxirans are examined in the oxidation of alkenes by molecular oxygen. The reactivities of various epoxidising agents are discussed. A list of 87 references is included.

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I. INTRODUCTION

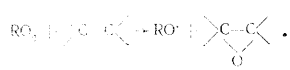
Direct oxidation of unsaturated compounds with molecular oxygen[1] is most promising for obtaining oxirans, which are used as monomers for the production of polyurethanes, stereospecific polymers, various additives, surface-active agents, and other important chemical products. The problem of establishing the mechanism of the epoxidation of alkenes by molecular oxygen therefore acquires great importance. It is now generally accepted that during direct oxidation alkene oxides are formed predominantly in the course of chain propagation by interaction between alkenes and various peroxy-radicals.

The present Review examines the structure of radical epoxidising agents, their reactivity, and the dependence of the selectivity of epoxidation on the structure of the initial alkene. Possible routes for epoxidation by molecular intermediate products are suggested. Catalytic epoxidation of alkenes by molecular oxygen and by hydroperoxides is not discussed here, since it has already been reviewed[2].

II. EPOXIDATION OF ALKENES BY ALKYLPEROXY-RADICALS

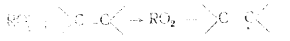
Most investigators accept that the main route to the formation of oxirans in the direct oxidation of alkenes is epoxidation of the latter by alkylperoxy-radicals[3-29].

The simplest reaction of this type occurs between a monomeric peroxy-radical and an alkene:



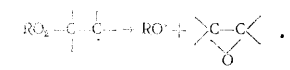
(1)

This takes place in two stages—addition of the peroxy-radical to the alkene to form a β-peroxyalkyl radical



(1′)

and breakdown of this radical into an oxiran and an alkoxy-radical



(1″)

The absence of stereospecificity in the epoxidation of alkenes by alkylperoxy-radicals[4,5,11,25] has been interpreted as evidence of intermediate formation of a β-peroxyalkyl radical. The probability of *cis–trans* isomerisation in this radical is determined by the relative rates of rotation about the C–C bond and of breakdown of the radical to form the oxiran.

The relative concentrations of *cis*- and *trans*-oxides of oct-4-ene among the reaction products depend[25] on the configuration of the alkene: more of the *cis*-oxide is obtained from *cis*-oct-4-ene, and more of the *trans*-oxide from the *trans*-alkene. This apparently indicates that the life of the β-peroxyalkyl radical is too short for the attainment of conformational equilibrium[25].

Effective activation energies for the overall reaction (1) have been determined for interaction of the methylperoxy-radical with substituted butenes in the gas phase at 100–130 °C[26] (Table 1). A similar value was obtained[87] for the gas-phase oxidation of ethylene: E_{eff} = 10 kcal mole^{-1}.

Table 1.

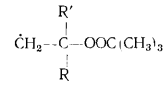
Alkene	2-Methylbut-1-ene	2-Methylbut-2-ene	2,3-Dimethylbut-2-ene
E_{eff}, kcal mole^{-1}	12.7±1.3	10.2±0.8	8.7±0.6

The addition of alkylperoxy-radicals to alkenes is reversible[28]. From the rate constants estimated from thermochemical data for the breakdown of β-peroxyalkyl radicals

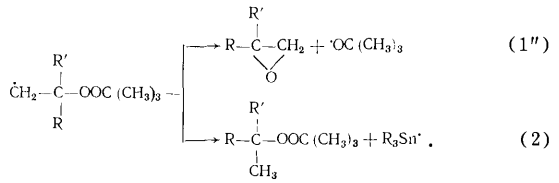
$$k_{1'} = 10^{11.5} \exp(-14\,000/RT);\quad k_{-1'} = 10^{13} \cdot \exp(-18\,000/RT)\quad (c^{-1}),$$

it can be concluded that the reverse reaction to (1′) begins to be significant only at high temperatures (above 300 °C)[28].

Rate constants for the decomposition of various β-peroxyalkyl radicals were determined experimentally[27]. The radicals were prepared independently by reaction between the corresponding brominated peroxides and hexamethyldistannane $(CH_3)_3Sn.Sn(CH_3)_3$ or a trialkylstannane R_3SnH in the presence of an initiator. Formation of the radicals was recorded by electron spin resonance at −70 °C. Further conversion of the β-peroxyalkyl radicals



was due to competition between two reactions—decomposition with formation of an oxiran (1″) and reduction in the presence of the trialkylstannane with formation of a dialkyl peroxide (2):

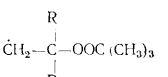
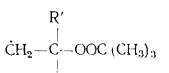
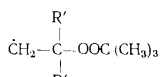


(1″)

(2)

The relative concentrations of the products—oxiran and dialkyl peroxide—gave the ratio of the rate constants of the two competing reactions k_1''/k_2. From the known value of k_2, rate constants were found[27] for the formation of oxirans in the decomposition at 25 °C of the β-peroxyalkyl radicals in Table 2.

Table 2.

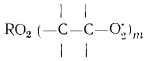
Radical*			
10^3k, s^{-1}	700	40	2

* R = CH_3 and R′ = H.

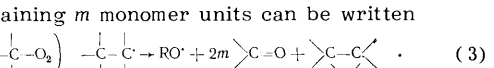
Thus the rate constant of reaction (1″) increases sharply with the number of substituent groups in the β-peroxyalkyl radical. The decomposition rate constants of such radicals are surprisingly large in absolute magnitude: the values obtained[27] exceed by many orders of magnitude those for the corresponding dialkyl peroxides (e.g. 10^{-6} s^{-1} for di-t-butyl peroxide in benzene at 80 °C[31]).

Indirect confirmation of the possibility that β-peroxyalkyl radicals decompose with the formation of oxirans was obtained as early as 1950[30]. Isobutene oxide (30 mole % based on the peroxide that had reacted) was detected in the thermal (100 °C) and photochemical decomposition of di-t-butyl peroxide, as a result of breakdown of the radical $(CH_3)_3COOC.(CH_3)_2CH_2$, formed in chain propagation[30].

Peroxy-radicals involved in epoxidation can react in either monomeric (RO_2) or polymeric

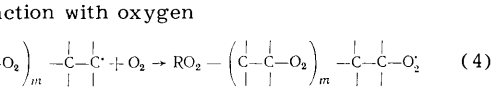


form[6,7,13-16,29]. Breakdown of the latter results in formation of an oxiran and a carbonyl compound in a single step, which for a radical containing m monomer units can be written



(3)

The length m of the carbon chain is determined by the relative rates of decomposition of the β-peroxyalkyl radicals (1″) or (3) and of reaction with oxygen



(4)

and depends on the structure of the initial alkene and the reaction conditions (Section IV).

Competition between reactions (1″) or (3) and (4) should lead to an inversely proportional dependence of the yield of oxiran on the concentration of molecular oxygen[10]:

$$\frac{w_{Ox}}{w_{Eth}} = \frac{1}{(A + B[O_2])} \qquad (4a)$$

where w_{Ox} is the rate of formation of the oxiran, w_{Eth} is the rate of consumption of the initial ethylenic compound, and A and B are constants containing the ratios of the rate constants of the primary stages. Decrease in yield (and rate of formation) of alkene oxides with increase in oxygen concentration over a certain range has been observed experimentally in the oxidation of a substituted norbornene (Fig. 1, curve *1*),[46] propene[59], and other alkenes[10,22,23], and is regarded as kinetic evidence of the formation of oxirans in the decomposition of β-peroxyalkyl radicals.

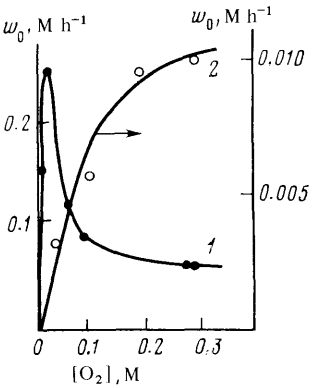
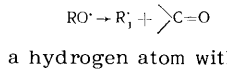


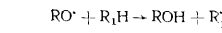
Figure 1. Dependence of initial rate of accumulation of alkene oxide on concentration of oxygen in the oxidation of methyl *exo*-2-methylbicyclo[2,2,1]hept-5-*endo*-carboxylate (a substituted norbornene) by molecular oxygen (50 atm) in benzene at 70 °C[46] in the presence of: 1) 0.01 M azoisobutyronitrile; 2) acetaldehyde (concerted oxidation).

Epoxidation (1″) should lead to the formation of equimolecular quantities of oxirans and monomeric or polymeric conversion products of alkoxy-radicals. Therefore some information on the course of such reactions in the complicated multistage oxidation of alkenes can be obtained by tracing the fate of such radicals formed in the epoxidation step. Three possible types of conversion are considered—(i) unimolecular decomposition with formation of an aldehyde and an alkyl radical[2,4,8,67]



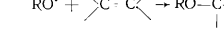
(5)

(ii) detachment of a hydrogen atom with formation of an unsaturated alcohol (in the case of an allylic alkoxy-radical) or a polymer containing a terminal hydroxy-group[4,8-10,20,32,67]



(6)

and (iii) addition at the double bond of the initial alkene[8-10,32]



(7)

In some cases (when epoxidation of alkenes is the main source of alkoxy-radicals) equivalence has been established

between the quantities of oxirans and conversion products of the radicals[3,8,9]. However, attempts to draw up such a balance have not always been successful. Thus decomposition should not be the only conversion undergone by alkoxy-radicals: in the presence of hydrocarbons containing reactive carbon–hydrogen or ethylenic bonds reaction (6) or (7) can compete successfully with unimolecular decomposition (5)[6,7] (especially in the case of primary and secondary alkoxy-radicals). In most work on the oxidation of alkenes however, unsaturated alcohols have been either detected in insignificant quantities or completely absent from the reaction products (Table 3).

Table 3. Oxidation of alkenes at 60–70 °C[8,9]*.

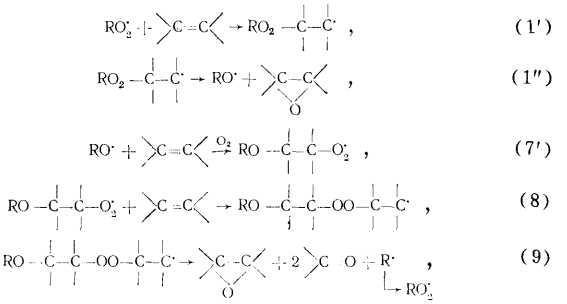
Alkene	β, %	10^3[Ox], moles	10^3[Alc], mole	10^3[Ke], moles	j	k	l
But-2-ene	4.5	2.31	0	3.27	4.00	7.78	2.18
2-Methylbut-2-ene	4.2	1.94	0.53	3.36	5.00	9.72	2.18
2,3-Dimethylbut-2-ene	4.7	3.06	0.58	4.31	6.00	11.66	2.26
Isobutene	4.5	3.39	0	2.82	4.00	6.98	1.60
Hex-1-ene	3.7	0.86	0.59		6.00	11.76	2.37
Cycloheptene (Ref.73)	5.5	2.04	1.55	0	7.00	13.81	2.00

* Here β represents the degree of conversion, Ox the alkene oxide, Alc an unsaturated alcohol, and Ke carbonyl compounds containing fewer carbon atoms than in the initial alkene. The composition of the macromolecular products $(C_jH_kO_l)_{m_i}$ was determined from elementary analysis; m_i is the number of monomer units in the polymer molecule.

The hypothesis that alkoxy-radicals are consumed mainly by addition to the double bond of the alkene is contradicted by the experimental observation that the rate of abstraction of a hydrogen atom from propene, determined for the t-butoxy-radical, exceeds about thirtyfold the rate of addition of this radical to propene[32] and other alkenes[31]. Furthermore, elementary analysis[8,9] indicates that the composition of the macromolecular products from several alkenes approximates to the empirical formula $C_nH_{2n}O_2$ (Table 3), which indicates that monomeric groups of peroxide character predominate in the polymer.

From the stoichiometry of the epoxidations (1) and (3) it may be expected that equimolecular quantities of alkene oxide and total conversion products of the epoxidising agent will be formed. This imposes a limit on the yield of oxiran, which theoretically should not exceed 50% based on the alkene consumed. In several cases, however, e.g. in the oxidation of cyclo-octene[34], norbornene derivatives[35–37,24], hexafluoropropene[38], "di-isobutene" (2,4,4-trimethylpent-1-ene)[39], and 2-methylpent-1-ene[33], the yield of alkene oxide exceeds the total yield of products formed from alkoxy-radicals, and reaches 70–80% based on the alkene that has reacted.

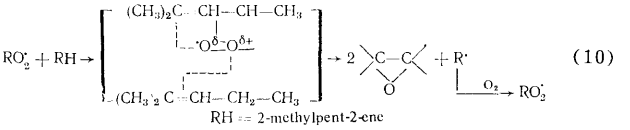
Except in the early work, in which direct incorporation of an oxygen molecule at the double bond of the alkene was assumed, as e.g. for di-isobutene[39], the observed regularities are mostly explained in terms of various radical epoxidation reactions having one fundamental common feature: regeneration of the $R\dot{O}$ (or $RO_2\dot{}$) radical carrying the chain oxidation is postulated in the epoxidation step. Thus the sequence of reactions



(1′) (1″) (7′) (8) (9)

provides a description of the kinetics of the oxidation of styrene derivatives[6,13], and gives theoretical maximum yields of alkene oxides up to 66%. This scheme of oxidation is applicable only to alkenes containing no reactive hydrogen atoms, for which chain propagation involves mainly addition of radicals at the double bond of the alkene and breakdown of the resulting polymeric radicals.

The composition of the oxidation products of 2-methylpent-2-ene, which is characterised by reactions involving abstraction of a hydrogen atom[33], can be explained by introducing into the scheme another epoxidation reaction

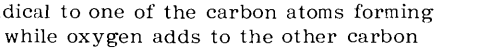


RH = 2-methylpent-2-ene (10)

which like reaction (9) leads to regeneration of the peroxy-radical. Scheme (10) involves polarisation of the dioxy-bond in an allylic peroxy-radical by interaction of the electron of the latter with the π-electrons of the double bond. This facilitates migration of the oxygen atom to the double bond and detachment of the second oxygen atom by an adjacent alkene molecule.

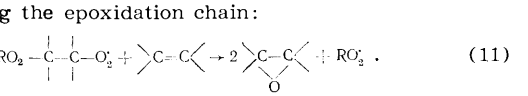
The high yield of oxides of norbornene derivatives, in particular of cyanonorbornene (~ 70% based on the alkene consumed)[35–37], cannot be explained by the above reactions (9) and (10), since structural features of norbornene make formation of allylic peroxy-radicals improbable[24,35,41] (the usual delocalisation of electron density in the radical formed by detachment of an α-hydrogen atom is difficult). Furthermore, the carbonyl compounds whose formation is implied by reaction (9) do not exceed 10% of the alkene that has reacted in the oxidation of norbornene derivatives.

We have suggested a mechanism[35,42] in which the epoxidising agent is a peroxy-radical formed by addition of a chain-carrying radical to one of the carbon atoms forming the double bond, while oxygen adds to the other carbon atom:



(1‴)

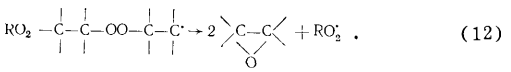
Such a radical reacts with the initial cyanobornene to form two molecules of the alkene oxide and regenerate the peroxy-radical carrying the epoxidation chain:



(11)

Overall, reaction (11) is energetically advantageous[42]. It

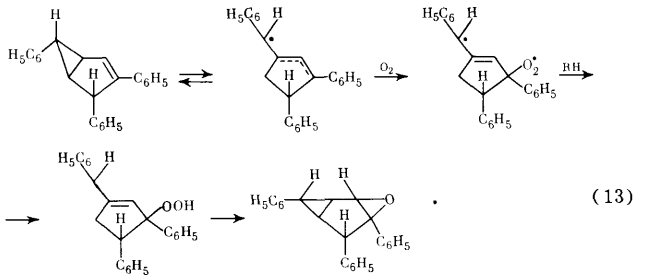
may take place not in a single stage but by formation and subsequent breakdown of a β-peroxyalkyl radical:



(12)

The mechanism of epoxidation suggested for derivatives of norbornene is also the most probable mode of formation of hexafluoropropene oxide[38], the yield of which reaches 80% based on the alkene that has reacted.

Yet another scheme of epoxidation was suggested in work[40] on the thermal oxidation of a bicyclo[3,1,0]hex-2-ene:



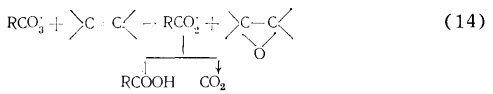
(13)

In this case the alkene oxide is formed by the breakdown and rearrangement of a hydroperoxyalkyl radical. The reaction sequence (13) was assumed by analogy with the published mechanism of thermal *exo–endo* isomerisation of bicyclo-compounds. However, oxidation of this bicyclo[3,1,0]hex-2-ene was conducted in xylene at temperatures above 100 °C, so that peroxy-radicals of xylene could have been the epoxidising agents, a possibility that was not considered[40]. Later other workers[19] published a study of the oxidation of conjugated dienones in cumene and in xylene at 120–130 °C, in which results were obtained indicating that under these conditions epoxidation involved peroxy-radicals of these solvents.

It must be noted that decomposition of hydroperoxyalkyl radicals has been assumed as the mode of formation of alkene oxides in the high-temperature (~ 400 °C) oxidation of alkenes in the gas phase[70–72].

III. EPOXIDATION OF ALKENES BY ACYLPEROXY-RADICALS

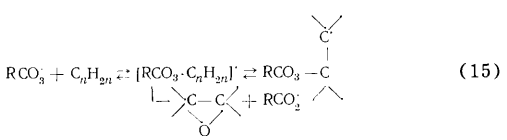
The epoxidation of alkenes by acylperoxy-radicals



(14)

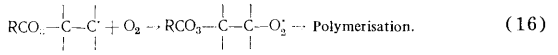
has an important role in systems in which aldehydes are formed as reactive intermediates. Reaction (14) has been studied in detail on the concerted oxidation of alkenes and aldehydes, a relatively simple process in which acylperoxy-radicals are the sole radical epoxidising agents[43–47,49,50,54]. The effective rate constant of reaction (14) determined for the concerted oxidation of nonene and benzaldehyde is 18000 M^{-1} s^{-1} at 90 °C[47]. The first stage of this reaction is assumed to be addition of acylperoxy-radicals at the double bond of the alkene.

One of the two views held concerning the structure of the radical adduct is that[43–45] reaction between acylperoxy-radicals and alkenes involves intermediate formation of a π-complex radical (as in the interaction of peracetic acid with propene[48]). The suggested general scheme of epoxidation[46]



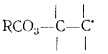
(15)

indicates that the initially formed π-complex $[RCO_3.C_nH_{2n}]^{\cdot}$ can react in two ways: it can decompose with formation of an oxiran or rearrange with fission of the π-bond. The latter process leads to subsequent formation of polymeric products:

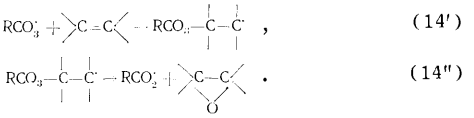


(16)

The alternative view[47] does not exclude the possibility of initial formation of a π-complex between radical and alkene. However, its concentration is considered[47] to be far lower than that of acylperoxy-radicals: a π-complex, even if formed, would rearrange rapidly into a β-peroxyalkyl radical



Thus formation of a complex is not a stage determining the macrokinetics of the process, and the mechanism of epoxidation by acylperoxy-radicals is assumed to resemble that by alkylperoxy-radicals:



(14′)

(14″)

The kinetics of the concerted oxidation of alkenes and aldehydes can be described on both views.

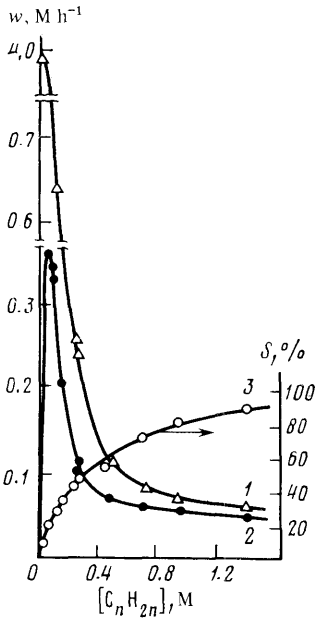


Figure 2. Effect of concentration of non-1-ene in chlorobenzene at 90 °C[47] on: 1) rate of consumption of benzaldehyde; 2) rate of accumulation of nonene oxide; 3) variation in yield of nonene oxide based on the benzaldehyde that has reacted.

Above a certain limiting value the alkene concentration ceases to affect the rate of accumulation of oxiran. Such a relation has been observed in the concerted oxidation of propene[45] and of nonene[47] with aldehydes (Fig. 2). In terms of

the hypothetical formation of an intermediate complex radical the explanation is that at a certain alkene concentration all acylperoxy-radicals are bound in the complex, and further increase in the alkene concentration leads to no increase in the concentration of the intermediate complex and hence in the rate of formation of the oxiran[45].

However, attainment of a limiting rate of epoxidation is not unequivocal evidence of existence of the complex $[RCO_3.C_nH_{2n}]_{\sim}$. This relation can be explained by compensation of the increase in rate of epoxidation due to increase in alkene concentration by decrease in the steady-state concentration of $RCO_{3\sim}$ radicals as a consequence of reaction (14')[47]. Thus this reaction produces a linear loss of such radicals. The dimeric (polymeric) peroxy-radical $MO_{2\sim}$ thus formed does not undergo the exchange reaction during development of the primary chain:

$$MO_{2\sim}^{\cdot} + RCHO \xrightarrow{O_2} RCO_{3\sim}^{\cdot} + MOOH. \qquad (17)$$

In the concerted oxidation of alkenes and aldehydes the dependence of rate of epoxidation (and yield of oxiran) on the oxygen concentration is similar to that observed for the oxidation of saturated compounds. Thus the rates of formation of the oxides of propene[45] and of a substituted norbornene[46] in the concerted oxidation of these alkenes with acetaldehyde increase continuously with the concentration of molecular oxygen up to a certain value, after which they cease to depend on this concentration (Fig. 1, curve 2).

Thus the dependence of rate of epoxidation on oxygen concentration changes qualitatively with the nature of the epoxidising agent (as mentioned above, a fall in rate with increase in oxygen concentration over a certain range has been observed for reactions of alkylperoxy-radicals[10,46]). One explanation for this difference is that reaction (16) with oxygen is improbable for a π-complex radical devoid of a free valency localised on a carbon atom[45]. Hence the epoxidation of alkenes by acylperoxy-radicals does not involve the competition between breakdown of a π-complex and its interaction with oxygen that can produce a fall in yield of alkene oxide with increase in oxygen concentration.

If the direct precursor of the oxiran is a σ-bound not a π-complex radical, the near independence of the yield (and rate of formation) of the oxiran from the oxygen concentration is interpreted as due to the rate of reaction (14") exceeding the rate of reaction (16) in the competition for radicals of type $RCO_3-C-C_{\sim}$[49].

The ratio of the rate constants k_{16}/k_{14}" estimated for the concerted oxidation of valeraldehyde and cyclohexene[49] supports the hypothetical rapidity of unimolecular decomposition (14"). However, it was admitted[49] that the accuracy of such an estimate was low, since the ratio was determined from constants *A* and *B* in Eqn.(4a), although the yield of the cyclohexene oxide varied very little with the oxygen concentration.

The stereochemical consequences of epoxidation by acylperoxy-radicals also support the concept of formation of the oxiran in decomposition of a σ-bound radical (14") having a carbon–carbon single bond. The concerted oxidation of benzaldehyde separately with *cis*- and *trans*-but-2-ene[50] and also the oxidation of isobutyraldehyde with the stereoisomers of oct-2-ene[54] yield mixtures of the *cis*- and *trans*-oxirans. Two trends were distinguished[50,54] in this process—stereospecific epoxidation of alkenes by peroxy-acids[51–53] and non-stereospecific epoxidation by acylperoxy-radicals.

Reaction (14) is accepted as the main path to formation of the oxides of propene[55–57,59], unbranched nonene[58], and hexene[60] in the direct oxidation of these alkenes by molecular oxygen. Involvement of acetylperoxy-radicals in the epoxidation step in the oxidation of propene is confirmed by experiments on the concerted oxidation of propene with acetaldehyde in the presence of iminoxyl radicals at 150 °C[57,59]. Under these conditions oxidation of propene is inhibited by iminoxyl radicals, and the only processes that occur are the oxidation of acetaldehyde and the epoxidation of propene by acylperoxy-radicals.

Table 4.

$[O_2]$, vol.%	21	12	8.0	2.5
Propene	0.8	—	2.0	—
Isobutene	1.1	—	2.1	2.2
Propene / Acetaldehyde	0.51	0.51	0.52	—

* Oxidation was conducted in the presence of stable iminoxyl radicals.

If acylperoxy-radicals are the sole epoxidising agents, the stoichiometry of reaction (14) requires that the rates of formation of the oxidation products should satisfy the relation†

$$\alpha = w_{Ox}/(w_A + w_{CO_2}) \leqslant 1,$$

in which w_{Ox} and w_A are the rates of formation of oxide and acid respectively. Such a relation has indeed been observed in the concerted oxidation of alkenes and aldehydes[43–47,59]. In the direct oxidation of alkenes, however, e.g. of propene[59] and isobutene[23], the parameter α increases to ~ 2–2.2 with decrease in the oxygen concentration of the oxidising gas. Table 4 gives the values obtained for α.

These results indicate that epoxidation of alkenes when oxidised by molecular oxygen has a complicated mechanism and that several epoxidising agents are involved in the formation of alkene oxides (e.g. alkylperoxy-radicals, which exhibit an increase in yield of alkene oxides with fall in oxygen concentration).

IV. INFLUENCE OF STRUCTURE OF ALKENES AND PEROXY-RADICALS ON RATE OF EPOXIDATION

The relative rates of epoxidation of alkenes by peroxy-radicals depend on the structure of the initial alkenes and on the reactivity of the double bond towards different epoxidising agents, as well as on the conditions of oxidation. We shall examine specific examples of the formation of alkene oxides involving various types of peroxy-radicals. Unfortunately, rigorous quantitative comparison of reaction rate constants is impossible because of the lack of appropriate data (different workers conducted oxidation under conditions that could not be compared, in several cases rates of initiation and chain-termination rate constants were not determined, etc.).

† The acid and carbon dioxide are products of further conversion of the alkylperoxy-radical, and are formed also in parallel chain oxidation reactions of aldehydes, e.g.

$$RCO_3^{\cdot} + RH \rightarrow \begin{cases} RCO_3H \\ \rightarrow RCO_2H. \end{cases}$$

The epoxidation of propene by peroxy-radicals formed in the oxidation of various compounds—aldehydes, butan-2-one, alkylated arenes, and saturated hydrocarbons—exhibits (Table 5)[43] clear selectivity of propene towards the epoxidising agents: the yield of methyloxiran is several times higher in the presence of acylperoxy-radicals than in epoxidation by peroxy-radicals e.g. of cumene or ethylbenzene. These results are consistent with experiments showing[62] that at 90 °C propene undergoes hardly any epoxidation by peroxy-radicals of ethylbenzene, whereas cyanoisopropylperoxy-radicals under the same conditions give only ~ 1% yield of methyloxiran calculated on the epoxidising compound.

Epoxidation by acyl- and alkyl-peroxy-radicals has been compared[46] in the oxidation of methyl *exo*-2-methylbicyclo.[2,2,1]hept-5-ene-*endo*-carboxylate by molecular oxygen in the presence of an initiator and in the concerted oxidation of this ester with acetaldehyde. The rate of formation of the alkene oxide via acylperoxy-radicals exceeded that via alkylperoxy-radicals by factors of ~ 30–40. Similar results have been obtained for the direct and concerted oxidation of cyclohexene[8,49]: whereas the former leads mainly to the formation of cyclohexenyl hydroperoxide (negligible quantities of cyclohexene oxide were detected), in the concerted oxidation of this alkene with valeraldehyde the oxiran becomes the main oxidation product.

Table 5. Yield S of alkene oxides calculated as a percentage of compound consumed.

Compound	t, °C	S, %	Compound	t, °C	S, %
Acetaldehyde	55—80	30.0—70.0	Butane	145	11.0
Propionaldehyde	70	50.0	Cumene	130	13.4
Butan-2-one	145	96.0	Ethylbenzene	120—140	15.0

The greater epoxidising power of acylperoxy- than of alkylperoxy-radicals can be explained in terms of the relative rates of the two competing reactions[49]—addition of peroxy-radicals to the ethylenic double bond

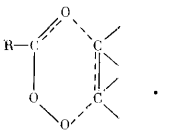
$$RCO_3^{\cdot}\ (\text{or}\ RO_2^{\cdot}) + \rangle C{=}C\langle \rightarrow RCO_3{-}\overset{|}{C}{-}\overset{|}{C}^{\cdot}\ (\text{or}\ RO_2{-}\overset{|}{C}{-}\overset{|}{C}^{\cdot}) \qquad (14')$$

and abstraction of an α-hydrogen atom relative to this bond

$$RCO_3^{\cdot}\ (\text{or}\ RO_2^{\cdot}) + RH \rightarrow R^{\cdot} + RCO_3H\ (\text{or}\ RO_2H)\ . \qquad (18)$$

The ratio of the rate constants of reactions (14′) and (18) for the interaction of the acetylperoxy-radical with cyclohexene exceeds the ratio for that of the cyclohexenylperoxy-radical by a factor of 30. This was attributed[49] to better stabilisation of the partial positive charge induced on the alkene in the transition state corresponding to addition of acylperoxy-radicals than in that arising on abstraction of a hydrogen atom. Such behaviour of acylperoxy-radicals will explain the high yields of alkene oxide obtained with respect not only to the alkene consumed but also to the organic compound introduced (Table 5).

In terms of scheme (15), which involves formation of π-complex radicals, the higher rates of epoxidation of alkenes by acylperoxy-radicals are explained[46] by stabilisation of π-complexes of alkenes with the latter radicals due to formation of six-membered structures of the type



Because of the relatively greater stability of such a complex with acylperoxy-radicals the equilibrium (15) will be displaced to the left, and it appears that only breakdown of the complex into the alkene oxide and the $RCOO_2^{\cdot}$ radical will take place[46].

Hypotheses[46,49] advanced to explain the great epoxidising power of acylperoxy-radicals are not inconsistent, since they concern different primary stages in the oxidation of alkenes. However, the epoxidation of alkenes by such radicals is not effective in all cases. Thus chloromethyloxiran could not be obtained at all by the concerted oxidation of acetaldehyde and allyl chloride (at 70–100 °C)[64]. Comparison of the reactivities of several hydrocarbons towards acetylperoxy-radicals shows that the rate of epoxidation depends significantly on the nature of the substituent adjacent to the double bond in the alkene[63,64]. This is illustrated by Table 6, in which w_0 is the initial rate of formation of the oxiran; the rate of chain initiation is in all cases 0.039 mM s^{-1} at 90 °C and 50 atm.

Table 6.

Alkene	Propene	Styrene	Cyclohexene
$10^5 w_0$, M s^{-1}	47	2.6	6.4
$10^2 k_2/k_6^{1/2}$, $M^{1/2}$ $s^{-1/2}$	24	1.3	3.3

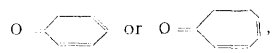
Table 7. Rates of formation w and yields S (based on alkene that has reacted) of alkene oxides in the action of isobutylperoxy-radicals on alkenes at 120 °C.[20]

Alkene	$10^6 w_0$, M s^{-1} (120° C)	S, %
α-Methylstyrene	16	86.5
Styrene	29	86
Propene	1.65	30
2,3-Dimethylbut-2-ene	1.55	38
Hex-1-ene	0.42	11.5

The epoxidising power of alkylperoxy-radical also is strongly dependent on the structure of the alkene and the conditions of oxidation. Thus epoxidation of cyanonorbornene—an alkene containing a reactive double bond (due to deformation of bond angles at the carbon atoms forming the double bond[65])—by peroxy-radicals of alkylarenes is observed even at 80 °C.[42] Under these conditions, however, the peroxy-radicals of ethylbenzene, as noted above, cause hardly any epoxidation of propene, an alkene containing a less reactive terminal double bond[43,62]. Epoxidation of propene by peroxy-radicals of alkyl groups—t-butyl[20] and apparently allyl[59]—begins to occur at an appreciable rate only at higher temperatures (120–150 °C—Table 7). Similarly, in the gas-phase oxidation of propene epoxidation by alkylperoxy-radicals becomes the predominant mode of formation

of methyloxiran only at high temperatures (above 350 °C). Under these conditions methyloxiran and acetaldehyde are formed simultaneously[66] (not consecutively, as would have been observed in epoxidation by acylperoxy-radicals).

Another illustration of the selectivity of epoxidation by alkylperoxy-radicals is the oxidation of conjugated dienones and diene ethers in cumene or xylene at 120–130 °C, when peroxy-radicals of the solvents act as epoxidising agents[19]. Cumenylperoxy-radicals react with conjugated alkenes, e.g.



to give oxides of the alkenes in high (50–95%) yields. However, these radicals do not epoxidise molecules containing isolated double bonds or cross-conjugated systems such as



Two factors govern selectivity according to the above mechanisms of epoxidation of alkenes by alkylperoxy-radicals. The first is the ratio of the rate constants of the two reactions between these species—addition at the double bond (1′) and (14′) and detachment of a hydrogen atom (18)—the kinetic consequences of competition between reactions (1′) and (18) having been examined first in 1958[63] and also subsequently[7–10,20,49]. Selectivity of epoxidation of various alkenes by t-butylperoxy-radicals in an inert atmosphere at 120 °C (Table 7) has in particular been related[20] to three factors—(*a*) the reactivity of the double bond (which varies with the substituents attached to the ethylenic carbon atoms), (*b*) the number of hydrogen atoms located α to the double bond (the greater the number of allylic hydrogen atoms the more rapid the detachment of a hydrogen atom (18), which competes with addition), and (*c*) characteristics of the allylic hydrogen atoms (whether primary, secondary, etc.). Table 7 shows that the maximum yield of alkene oxide is obtained with styrene derivatives, which interact with t-butylperoxy-radicals almost solely by addition of the latter at the double bond.

Table 8. Ratios $k_{1'}/k_r^{1/2}$ and $k_{18}/k_r^{1/2}$ $M^{-1/2}$ $h^{-1/2}$ at 70 °C.[9]

Alkene	$k_{1'}/k_r^{1/2}$	$k_{18}/k_r^{1/2}$	Alkene	$k_{1'}/k_r^{1/2}$	$k_{18}/k_r^{1/2}$
Propene	0.014	0.013	Isobutene	0.051	0.012
But-1-ene	0.017	0.019	2-Methylbut-2-ene	0.111	0.102
trans-But-2-ene	0.033	0.040	2,3-Dimethylbut-2-ene	0.25	0.67

Published results[9] also permit comparison of the ratios $k_{1'}/k_r^{1/2}$ and $k_{18}/k_r^{1/2}$ (in which k_r is the rate constant of quadratic recombination of peroxy-radicals) for the interaction of alkenes with allylic peroxy-radicals of the same structure as the initial alkene. Comparison was based on the postulate that variation of these parameters was due mainly to change in $k_{1'}$ and k_{18}. Although this approximation is not entirely accurate (as was admitted[9]), a general tendency for the reactivity of alkenes to vary with their structure can be quite definitely traced (Table 8). Maximum values of $k_{18}/k_r^{1/2}$ were obtained for alkenes having the largest number of allylic hydrogen atoms; the ratio $k_{1'}/k_r^{1/2}$ increases with the number of substituents attached to the ethylenic carbon atoms in the alkenes investigated.

Data on the influence of temperature on competition between reactions (18) and (1′) are few and disconnected. An example is provided by chain-propagation rate constants obtained for the oxidation of cyclohexene[68]:

$$k_{18} = 4.8 \cdot 10^6 \exp[(-6300 \pm 300)/RT] \ (M^{-1}\,s^{-1})$$
$$k_{1'} = 1.2 \cdot 10^8 \exp[(-14000 \pm 600)/RT] \ (M^{-1}\,s^{-1}).$$

These results show that rise in temperature should lead to a relative increase in the rate of addition of peroxy-radicals to the double bond in cyclohexene.

Table 9.

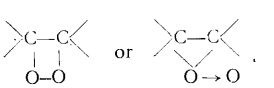
Alkene	*t*, °C	$k_4/k_{1''}$, M^{-1}	Alkene	*t*, °C	$k_4/k_{1''}$, M^{-1}
2,3-Dimethylbut-2-ene	50	32	But-2-ene	70	110
Cycloheptene	60	34	2-Methylbut-2-ene	60	150
Cycloheptene (*in benzene*)	90	25	α-Methylstyrene	50	5.9–11.0
2-Methylpent-1-ene	70	110	Styrene	50	53–154

The second factor governing selectivity of epoxidation is the ratio of the rates of the two conversions undergone by β-peroxyalkyl radicals—decomposition with formation of alkene oxide (1″) and reaction with oxygen (copolymerisation of alkene with oxygen) (4)—competition between which has already been discussed in connection with the influence of oxygen concentration on the yield of alkene oxides (Section II). Table 9 shows that the ratios of the rate constants $k_4/k_{1''}$ for various alkenes differ more than tenfold (cf. styrene and ethylene derivatives)[10]. This is due to variation in both k_4[31] and $k_{1''}$, the latter of which increases[27] from 2000 to 700000 s^{-1} with the number of methyl groups in the β-peroxyalkyl radical. It is noteworthy also that values of $k_{1''}$, estimated from the ratio $k_4/k_{1''}$ (using values of k_4 from Ref. 31) lie in the range 10^4–10^6 s^{-1}. This is consistent with results obtained for the decomposition of β-peroxyalkyl radicals prepared from the corresponding bromo-peroxides[27].

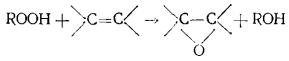
The ratio $k_4/k_{1''}$ diminishes with rise in temperature, since estimated[26] activation energies of decomposition of β-peroxyalkyl radicals are 14–15 kcal $mole^{-1}$, whereas addition of R_2 radicals to oxygen takes place with almost zero activation energy[4]. As a consequence, oxidative polymerisation predominates at low temperatures[61,69], but rise in temperature produces an increase in yield of monomeric decomposition products of the radicals—carbonyl compounds and alkene oxides[13,61].

V. EPOXIDATION OF ALKENES BY INTERMEDIATE MOLECULAR OXIDATION PRODUCTS

We have hitherto examined known routes to the formation of alkene oxides involving free radicals. An alternative view found in the literature (the earliest idea on the mechanism of epoxidation) regards the process as involving intermediate molecular oxidation products—hydroperoxides[73–75] and cyclic peroxides having the structure[39,76,77]



However, later work showed[4] that alkene oxide and hydroperoxide are formed in parallel in the oxidation of cyclohexene, and the rate of formation of the oxiran far exceeds the rate of epoxidation by the hydroperoxide

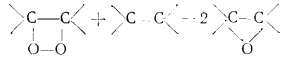


(19)

in the absence of a catalyst. Nor were alkene oxides detected in the thermal decomposition of hydroperoxides in the presence of alkenes[78,79].

The role of cyclic peroxides (dioxetans) in the mechanism of the oxidation of alkenes, and in epoxidation in particular, has recently been the subject of renewed attention[80], for experimental results have been obtained indicating the possibility of their formation in the oxidation of certain alkenes by molecular oxygen[81]. The chemiluminescence method suggests[81] that dioxetans are formed by a radical process in chain-propagation reactions, not by direct addition of oxygen at the double bond of the alkene, as had earlier been postulated[76]. Chain formation of dioxetans has been assumed[82] also in the oxidation of pent-1-ene.

An epoxidising role of dioxetans



(20)

has been postulated for the oxidation of norbornene[83] and of 7,7-binorbornylidene[84] by singlet oxygen under conditions such that the rate of radical oxidation by triplet molecular oxygen is negligible. However, the hypothetical involvement of dioxetans in epoxidation has not yet found direct experimental confirmation. Detailed investigation of the dependence of the yield of alkene oxide on the nature and concentration of the sensitiser used and also on additions of inhibitors of free-radical reactions in the oxidation of biadamantylidene[85] indicated the occurrence of two independent processes—(i) formation of a dioxetan by a molecular process and (ii) radical epoxidation involving sensitiser molecules.

Results have been obtained recently[80] indicating a molecular mechanism of epoxidation in the oxidation of alkenes. A solution of styrene in chlorobenzene with additions of a polymeric product (of the copolymerisation of styrene with oxygen) when oxidised gives a nearly 100% yield of styrene oxide calculated on the styrene that has reacted (Fig. 3)#. Additions of an inhibitor of free-radical reactions do not halt epoxidation. Table 10 shows the changes in concentration (molarity) of styrene, benzaldehyde, and styrene oxide 20 min after addition of the inhibitor (0.01 M 1-naphthol) to the reaction mixture in the oxidation of styrene§. It is evident that the oxide accumulates as the sole reaction product under the inhibited conditions of oxidation.

It has been shown also[80,86] that such molecular epoxidising agents as hydroperoxides and peroxy-acids are absent from the reaction mixture, and that the polymeric product is a precursor of styrene oxide in the sequence of primary oxidation stages. These results suggest that oxygen transfers from the polymer molecule, the "matrix", to the double bond of the alkene. The structure of the oxygen-containing polymer is being further investigated. Perhaps the active agent in epoxidation is the dioxetan group



on the polymer matrix[80].

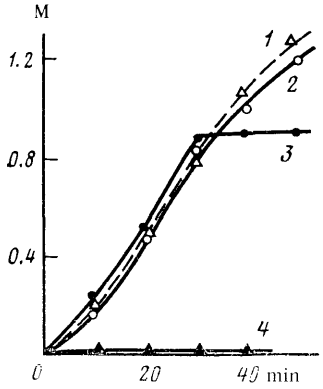


Figure 3. Rate curves for the oxidation of styrene in chlorobenzene solution with addition of 30 vol.% of a styrene–oxygen copolymer[80] at 120 °C: 1) consumption of styrene ($[RH]_0-[RH]_{inst}$); 2) accumulation of styrene oxide; 3) accumulation of benzaldehyde; 4) accumulation of polymeric product.

Table 10.

Styrene	oxide Styrene	Benzaldehyde
1.25 — 1.00	0.42 — 0.62	0.30 — 0.32

Thus the above results[80,81,86] indicate that formation of alkene oxides involving peroxy-radicals is not the sole mode of epoxidation. Under certain conditions a molecular mechanism makes a contribution to epoxidation. Its inclusion provides an explanation of facts that are not covered in generally accepted schemes of epoxidation.

Benzaldehyde is formed by decomposition of the polymeric product.

§ The initial concentration of styrene was 1.8 M, and that of the polymeric product 30 vol.%; the solvent was chlorobenzene, and the temperature 120 °C.

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Sterically Hindered Porphyrins

A.V.Bogatskii and Z.I.Zhilina

Data on the chemistry of sterically hindered porphyrins as well as dimeric and trimeric prophyrins are examined and described systematically. Attention has been concentrated on sterically hindered porphyrins as synthetic models of natural oxygen-transferring agents—haemoglobin and myoglobin.
The bibliography includes 94 references.

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I. INTRODUCTION

Iron-porphyrins are classified in terms of their functions as the prosthetic groups of an important class of proteins and enzymes—haemi- and haemo-proteins[1-3]. The main function of natural haemoproteins such as haemoglobin and myoglobin is based on their ability to combine reversibly with oxygen. The structures of haemoglobin[4] and myoglobin[5] have been determined by X-ray diffraction. The studies by Perutz and Kendrew showed that the iron-porphyrin complex is located in a hydrophobic "protein pocket". The iron atoms in the molecules of both proteins are coordinated to the four nitrogen atoms of protoporphyrin-IX and to the nitrogen atom of the imidazole ring in the histidine residue forming part of the polypeptide chain of the haemoglobin molecule. In oxygenation a second azial ligand (oxygen) is added. The decisive factor in the biological function of haemoproteins is the spin state of iron. In haemoglobin and myoglobin the Fe^{II} atom is pentacoordinate in the deoxy-form. The high-spin form has an ionic radius which is too large for the Fe^{II} atoms to be accommodated within the cavity of the porphyrin. The iron atom in the high-spin state lies outside the limits of the plane of the four nitrogen atoms of porphyrin towards the "proximal" imidazole.

Whereas the Fe^{II} atom is hexacoordinate, the low-spin iron atom of the diamagnetic oxyhaemoglobin or oxymyoglobin lies within the cavity in the porphyrin ring. It can be assumed that Fe^{II} oscillates very rapidly between these states and that the part of the protein molecule linked directly to the iron atoms via the "proximal" imidazole also undergoes rapid changes[6].

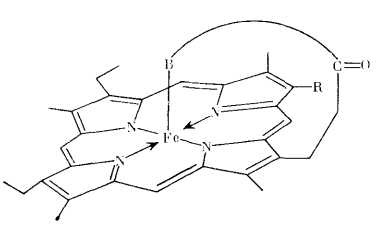
The nature of the regulation of the oxygen affinity, of the control of the axial binding, and of the means used by the protein to ensure the kinetic stability of the dioxy-form in haemoglobin and myoglobin can be most readily understood by obtaining and fully characterising model compounds which are capable of binding oxygen reversibly. In recent years the problem of such modelling has aroused much interest. Various teams of investigators have devoted their attention to problems of the modelling of natural haemoproteins based on metalloporphyrins.

In modelling account is usually taken of the following factors[7]: (1) the steric hindrance around the "active centre"; (2) the role of the "proximal" imidazole in coordination to the Fe^{II} atom in the 5-position; (3) the influence of the "distal" imidazole on the kinetic stability of the oxy-form of haemoglobin and myoglobin and the search for ways of modelling it; (4) the basicity of the "proximal" imidazole; (5) the characteristics of the stereochemistry of the "hydrophobic pocket" formed by the protein around haem and the search for ways of its chemical modelling.

By virtue of the advances in the development of bioorganic chemistry, a need has arisen for well-defined dinuclear metal complexes such as haemoerythrin, haemocyanine[6], and superoxide disnutase, which serve as models of various metalloenzymes[6,8]. Model systems which are of interest from the standpoint of the study of interionic interactions have also been synthesised[9,10]. Since 1973, the principal trend in the development of the chemistry of porphyrins has been the creation of model compounds on the basis of sterically hindered porphyrins. The present review is devoted to the analysis of the literature on this extremely interesting question published during the last seven years.

II. THE SYNTHESIS AND PROPERTIES OF STERICALLY HINDERED PORPHYRINS

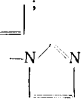
In contrast to haemoglobin and myoglobin which are capable of being reversibly oxygenated, simple iron-porphyrins are rapidly and irreversibly oxidised by atmospheric oxygen. Wang[11] was the first to establish that simple porphyrins can undergo reversible oxidation when they are placed in a specially prepared polymer film. Somewhat later, a series of papers were published[12-17] describing the reversible attachment of oxygen to Fe^{II}-porphyrins (I) in solutions at a low temperature. In these experiments, compounds (I) were modified in such a way that the base was covalently bound to the carboxy-groups in the porphyrin ring:



(I)

(a) R = H, B = $-NH(CH_2)_3-$  ;

(b) R = $-CH_2CH_2COOCH_3$, B = $-NH(CH_2)_3-$  ;

(c) R = $-CH_2CH_2CONH(CH_2)_3-$  , B = $-NH(CH_2)_3-$  ;

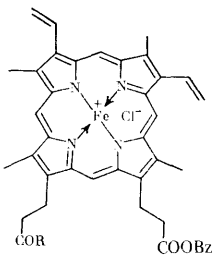
(d) R = $-CH_2CH_2COOCH_3$, B = $-O(CH_2)_3-$  ;

(e) R = $CH_2CH_2COO(CH_2)_3-$  , B = $-O(CH_2)_3-$  .

Pyrroporphyrin-*N*[3-(1-imidazolyl)propyl]amide (Ia) has been obtained[12] by treating pyrroporphyrin-XV [18] with 1-(3-aminopropyl)imidazole at room temperature in a solvent mixture (2:1:1 methylene chloride–acetone–pyridine); the amides (Ib) and (Ic) have been obtained[15] by treating the acid chloride of the monomethyl ester of mesoporphyrin-IX with 1-(3-aminopropyl)imidazole, while compounds (Id) and (Ie) [15] have been synthesised by treating the acid chloride of the monomethyl ester of mesoporphyrin-IX with 3-(3-pyridyl)-1-propanol.

In contrast to these methods, a number of workers[19–21] used the methyl ester of histidine and substituted histidine-containing peptides as ligands in iron-haemin. The peptides comprised the methyl ester of t-butoxycarbonyl-leucyl-histidine, the benzyl ester of t-butoxycarbonylhistidyl-leucylglycyl-*S*-benzylcysteine, and the benzyl ester of t-butoxycarbonyl-leucylhistidylalanyl-*S*-benzyloxycarbonyl-lysylglycyl-*N*-benzylcysteine[19–21].

A series of *C*-aminoacyl derivatives of haemin (IIb)–(IIf) have been obtained from the monobenzyl ester of haemin (IIa):[20]



(II)

(a) R=OH;

(b) R = Ala — OMe;

(c) R = His — OMe;

(d) R = Leu—His—OMe

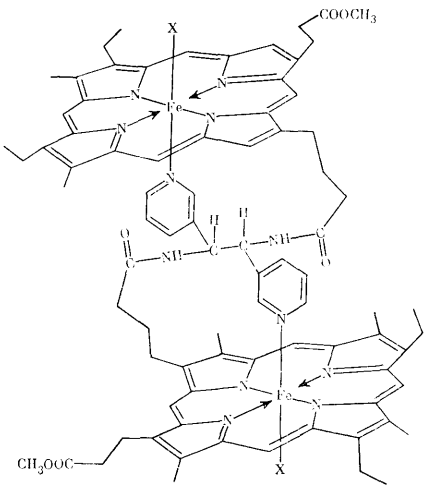
(e) R = Leu—His—Leu—Gly—Lys(Bz)—OBz

(f) R = Leu—His—Ala—Lys(Z)—Gly—Lys(Bz)—OBz.

Compounds (IIb)–(IIf) were synthesised by condensing the monobenzyl ester of haemin with the methyl esters of alanine and histidine and also with the *N*-unsubstituted di-, penta- and hexa-peptides enumerated above—by the mixed anhydride method involving interaction with ethyl chloroformate in dimethylformamide (DMF) in the presence of triethylamine. The bis-*C*-aminoacyl derivatives of haemin have been obtained analogously[19].

It has been shown[20] that the pentacoordinate complexes of iron-porphyrins, obtained by reducing compounds (IIe) and (IIf) with an aqueous solution of sodium dithionite in an atmosphere of nitrogen, are able to combine reversibly with oxygen in the course of 35–40 min at room temperature.

In order to investigate the interaction of haem molecules within a single conformational system, Traylor et al.[22] obtained the model compound (III) from the monomethyl ester of mesoporphyrin and 1,2-di-(3-pyridyl)ethylenediamine[23], in which two haem molecules are conformationally linked via the common central ethylenic linkage. Any change in the conformation of the "upper" iron-containing porphyrin ring must influence the conformation of the identical "lower" ring via this bond. Compound (III) combines reversibly with oxygen in solution, being converted into compound (IIIb), and reacts with carbon monoxide in two stages (in contrast to model monohaem compounds[24,25]), forming compound (IIIc): (a) X absent; (b) X = O_2; (c) X = CO.



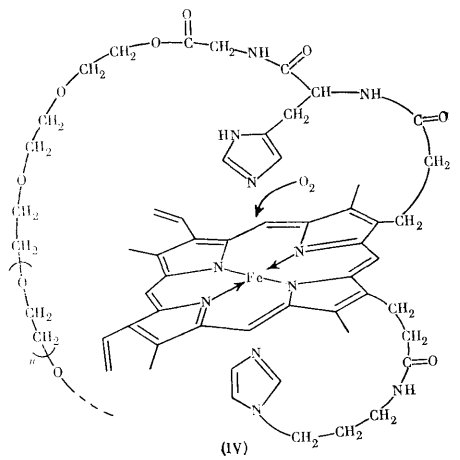
(III)

In 1977 German investigators[26] synthesised the haem polymer (IV) capable of reversible transfer of molecular oxygen. This haem polymer had the properties of the natural oxygen carrier—haemoglobin: high solubility in water, difficult irreversible oxidation of the oxygen complex by the functional polymer, and similarity to the "distal" imidazole. The principal initial polymers were poly(ethylene glycol)–bis-(glycine ester) (V) [27] and the polyurethane (VI) obtained from poly(ethylene glycol) (PEG) and di-isocyanate.

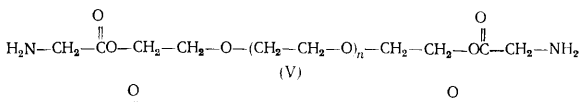
Di-t-butoxycarbonylhistidine was attached to the free amino-groups of polymers (V) and (VI) by means of liquid-phase peptide synthesis[27]. After the removal of the protecting group from histidine, poly(ethylene glycol)–bis(glycyl-histidylhaemin) (VII) and the histidylhaem derivative of the polymeric urethane (VIII) were obtained.

The histidine in the polymeric haemins (VII) and (VIII) is linked to the carboxy-group of haemin via the amide group. In this structure the optimum coordination of the imidazole nitrogen atom of histidine is sterically hindered. Consequently this histidine may be compared with the "distal" histidine in myoglobin and haemoglobin.

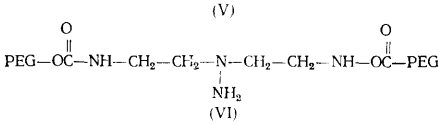
3-(1-Imidazolyl)propylamine has been attached to two carboxy-groups of the haem polymer (VII) by liquid-phase peptide synthesis[26] and compound (IV) was obtained. The imidazole residue in the polymeric haemin (IV) is optimally coordinated to the iron atom. In this haem polymer the oxygen coordination site is shielded both by histidine and by the synthetic polymer. The iron(II) complex of the haem polymer (IV) is readily soluble in water and combines reversibly with oxygen in solution. After frequent repetitions of the oxygen addition and liberation process, complex (IV) is oxidised to a haemin polymer, which, however, can be again reduced to compound (IV). The reversible oxygenation cycle is then again repeated.



(IV)



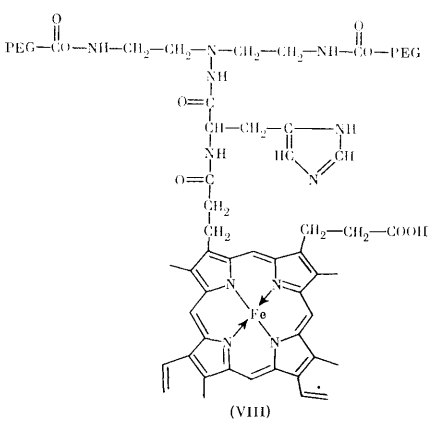
(V)



(VI)

Haem—His—Gly—PEG—Gly— His — Haem

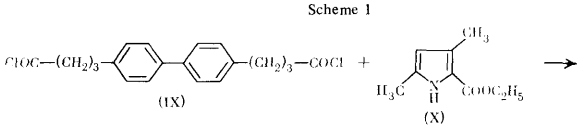
(VII)



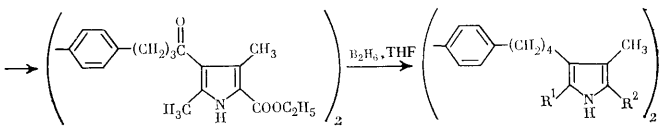
(VIII)

The copper and iron complexes of the first cyclophane (bridged) porphyrin compounds (XVI) and (XVII) were obtained for the first time by Diekman et al [28] from dipyrromethenes (XIV) linked by both ends of the aromatic chain. Friedel–Crafts acylation of 5-ethoxycarbonyl-2,4-dimethylpyrrole (X) [29] with the acid dichloride (IX) in the presence of aluminium chloride and nitrobenzene yielded dipyrrole (XI), [30] whose keto-group was reduced with B_2H_6 in tetrahydrofuran (THF) with formation of compound (XIIa): [31]

Scheme 1



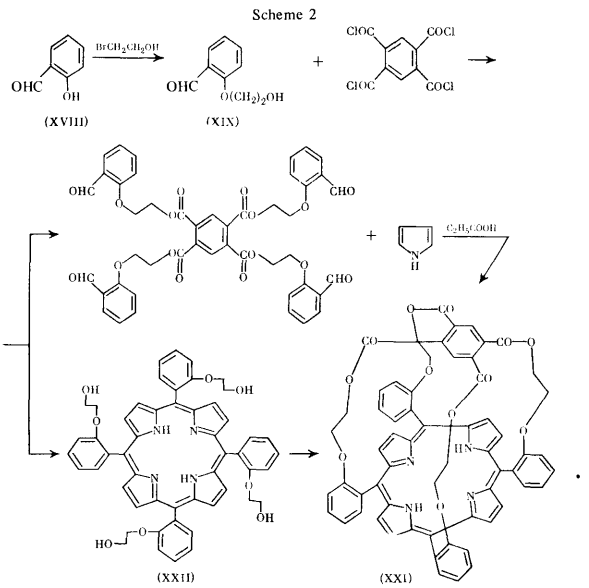
(IX) (X)



(XI) (XII)

(a) R^1=CH_3, R^2 = $COOC_2H_5$; (b) R^1=CH_3, R^2=$COOC_6H_5$; (c) R^1=CHO, R^2=$COOC_6H_5$; (d) R^1=CHO, R^2=COOH

Scheme 2

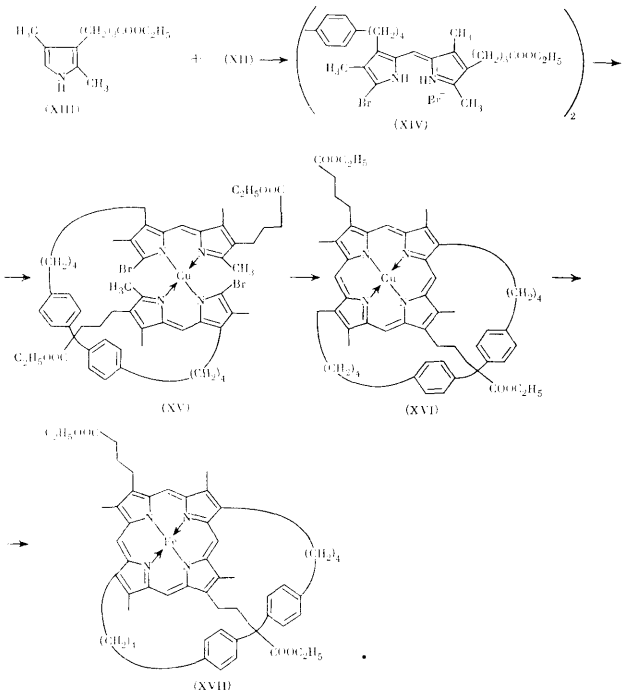


(XVIII) (XIX) (XXII) (XXI)

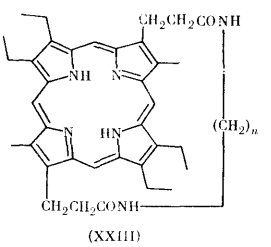
Transesterification with sodium benzilate and subsequent treatment with sulphuryl chloride in the presence of diethylamine then gave rise to the aldehyde (XIIc), the catalytic hydrogenolysis of which led to compound (XIId). [32,33] Condensation of the substituted pyrrole (XIId) with the substituted pyrrole (XIII) [34] in the acetic acid–hydrogen bromide mixture followed by bromination of the product led to the formation of dibromopyrromethene (XIV). [35] On treatment with copper acetate in the presence of ammonia, the latter forms the copper complex (XV), which cyclises on heating in xylene with formation of the copper complex of the cyclophane porphyrin (XVI). [36] The free porphyrin is formed from compound (XVI) under the influence of sulphuric acid. Complex (XVII), containing iron(III), was obtained from the free porphyrin by treatment with iron sulphate (Scheme 1).

The second cyclophane porphyrin (XXI), called the capped porphyrin, has been obtained by Baldwin and coworkers [37–39]. The crystalline iron(II) complex of this model undergoes reversible oxygenation in solution in pyridine or benzene containing *N*-methylimidazole; the oxygenation of the iron(II) complex of the model compound (XXI) in solution in pyridine requires 20 h. [38] The capped porphyrin (XXI) has been obtained [82] by the direct condensation of the tetra-aldehyde (XX) with pyrrole in propionic acid. The tetra-aldehyde (XX) has been obtained by alkylating salicylaldehyde (XVIII) with the aid of bromohydrin to the corresponding ester (XIX), which was converted into compound (XX) by interaction with pyromellitic acid chloride in a THF–triethylamine mixture [37] (Scheme 2). The capped porphyrin (XXI) has also been synthesised by esterifying compound (XXII) with pyromellitic

acid chloride[37]:

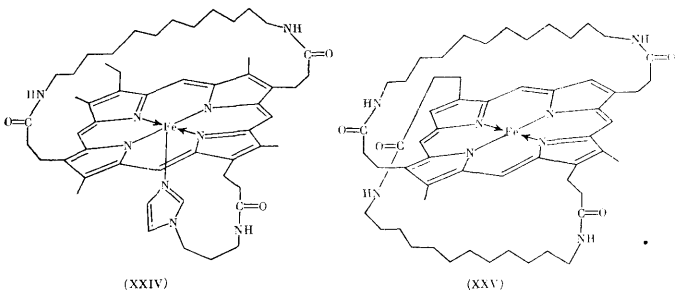


Japanese investigators[40–43] synthesised a series of cyclophane porphyrins (XXIII) with different lengths of the aliphatic bridge connecting the symmetrically located carboxy-groups of the propionic acid residues of the porphyrin:

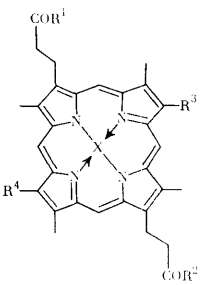


The interaction of 4,8-di-(2-carboxyethyl)-1,2,5,6-tetraethyl-3,7-dimethylporphyrin[44] with diamines $NH_2(CH_2)_nNH_2$, where n = 6, 7, 8, 9, 10, or 12, and also (for comparison) with propylamine in the presence of isobutyl chloroformate and triethylamine in THF under the conditions of high dilution, the reaction products being subsequently treated with zinc or iron acetate, yielded the corresponding complexes of cyclophane porphyrins[43].

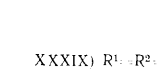
Compounds (XXIV) and (XXV), which are models of haemoglobin and myoglobin, have been obtained[45,46] from porphyrins in which the "bridges" form a belt around the porphyrin ring on either side of its plane. The necessary initial porphyrins (XXVI), (XXVII), and (XXVIII) were obtained via *ac*-biladienes[47]:

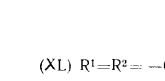


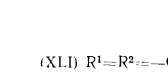
Scheme 3

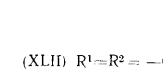


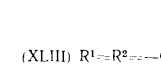
(XXVI) R^1 = OH, R^2 = OH, R^3 = R^4 = H, X = 2H;
(XXVII) R^1 = OH, R^2 = OH, R^3 = $COOC_2H_5$, R^4 = H, X = 2H;
(XXVIII) R^1 = OH, R^2 = OH, R^3 = $COOC_2H_5$, R^4 = $COOC_2H_5$, X = 2H;
(XXIX) R^1 = Cl, R^2 = Cl, R^3 = R^4 = H, X = 2H;
(XXX) R^1 = $-O(CH_2)_4C{\equiv}CH$, R^2 = $-O(CH_2)_4C{\equiv}CH$, R^3 = R^4 = H, X = 2H;
(XXXI) R^1 = $-O(CH_2)_4C{\equiv}CH$, R^2 = $-O(CH_2)_4C{\equiv}CH$, R^3 = R^4 = H, X = $Fe^{III}Cl$;
(XXXII) R^1 = R^2 = $-O(CH_2)_4C{-}C{\equiv}C{-}C(CH_2)_4O$, R^3 = R^4 = H, X = $Fe^{III}Cl$;
(XXXIII) R^1 = R^2 = $-O(CH_2)_4C{-}C{\equiv}C{-}C{-}(CH_2)_4O$, R^3 = R^4 = H, X = Cu;
(XXXIV) R^1 = R^2 = $-O(CH_2)_{12}O$, R^3 = R^4 = H, X = Cu;
(XXXV) R^1 = R^2 = $-O(CH_2)_{12}O$, R^3 = R^4 = H, X = 2H;
(XXXVI) R^1 = R^2 = $-NCH_3(CH_2)_5COCH_3$, R^3 = R^4 = H, X = 2H;
(XXXVII) R^1 = R^2 = $-NCH_3(CH_2)_5CO(CH_2)_5NCH_3$, X = 2H;
(XXXVIII) R^1 = R^2 = $-NH(CH_2)_{12}NH$, R^3 = R^4 = H, X = 2H;

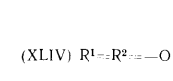
XXXIX) R^1 = R^2 = $-O(CH_2)_3$–  –$(CH_2)_3O$, R^3 = R^4 = H, X = 2H;

(XL) R^1 = R^2 = $-O(CH_2)_3$–  –$(CH_2)_3O$, R^3 = R^4 = H, X = 2H;

(XLI) R^1 = R^2 = $-O(CH_2)_3$–  –$(CH_2)_3O$, R^3 = R^4 = H, X = 2H;

(XLII) R^1 = R^2 = $-O(CH_2)_3$–  –$(CH_2)_3O$, R^3 = R^4 = H, X = $Fe^{III}Cl$;

(XLIII) R^1 = R^2 = $-O(CH_2)_3$–  –$(CH_2)_3O$, R^3 = R^4 = H, X = $Fe^{III}Cl$;

(XLIV) R^1 = R^2 = $-O(CH_2)_3$–  –$(CH_2)_3O$, R^3 = R^4 = H, X = $Fe^{III}Cl$;

(XLV) R^1 = R^2 = $-NH(CH_2)_{12}NH$, R^3 = $-CONH(CH_2)_3$–  ,

R^4 = H, X = 2H;

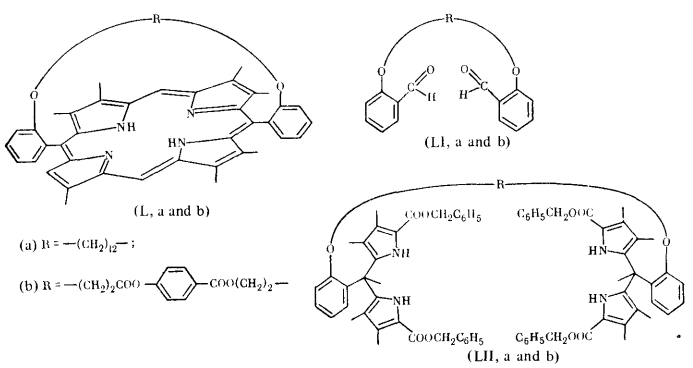
(XLVI) R^1 = R^2 = $-NH(CH_2)_{12}NH$, R^3 = $-COOC_2H_5$, R^4 = H, X = 2H;
(XLVII) R^1 = R^2 = $-NH(CH_2)_{12}NH$, R^3 = R^4 = $-CONH(CH_2)_{12}NHCO$, X = 2H;
(XLVIII) R^1 = R^2 = $-NH(CH_2)_{12}NH$, R^3 = R^4 = $-CONH(CH_2)_{12}NHCO$, X = $Fe^{III}Cl$;

(XLIX) R^1 = R^2 = $-NH(CH_2)_{12}NH$, R^3 = $-CONH(CH_2)_3$–  , R^4 = H, X = $Fe^{III}Cl$.

The acid dichloride (XXIX) was made to react with hex-5-yn-2-ol [48], which led to the formation of the corresponding diester (XXX). The oxidation of the iron(III) complex of the diester (XXXI) with copper acetate in the pyridine–ether mixture leads to the bridged porphyrin (XXXII).[49] When the metal-free diester (XXX) is oxidised, the copper complex of the bridged porphyrin (XXXIII) is obtained. Reduction of the latter yielded the porphyrin (XXXIV); its demetallation leads to compound (XXXV). The diamide (XXXVI) has been obtained[50] by the reaction of the acid dichloride (XXIX) with $CH_3NH(CH_2)_5COOCH_3$. When the diamide (XXXVI) is refluxed with t-BuOK in toluene, the bridged porphyrin (XXXVII) is obtained[50]. Condensation of the acid dichloride (XXIX) with 1,12-diaminododecane at a high dilution[43] leads to the bridged porphyrin (XXXVIII) and the reaction of the acid dichloride (XXIX) with 2,6-di(γ-hydroxypropyl)pyridine, 3,5-di(γ-hydroxypropyl)pyridine, and 3,5-di(γ-hydroxypropyl)dimethylpyridine yielded the bridged porphyrins (XXXIX)–(XLI) respectively[46]. The complexes (XLII)–(XLIV) have been synthesised by a standard method[51]. The cyclophane porphyrin (XLV) with a covalently bound ligand has been obtained[46] by the reaction of the acid chloride corresponding to compound (XLVI) with 3-aminopropylimidazole. A series of successive transformations of the diethyl ester of the tetracarboxylic acid (XXVIII) led to the formation[46] of the porphyrin (XLVII) in which two "bridges" are located on either side of the plane of the porphyrin ring system (Scheme 3). The introduction of iron[51] into the bridged porphyrins (XLV) and (XLVII) made it possible to obtain the models (XLVIII) and (XLIX) of the active centres in myoglobin and haemoglobin.

The bridged ("belted") porphyrins (L) (Scheme 4) have been obtained[52] by the direct condensation of the dialdehydes (LI, a and b) with the benzyl ester of 3,4-dimethylpyrrole-2-carboxylic acid in the presence of hydrogen chloride with subsequent catalytic debenzylation of the intermediate (LII).[53] The dialdehyde (LIa) has been synthesised by the condensation of salicylaldehyde with 1,12-dibromododecane and the dialdehyde (LIb) has been obtained from *o*-(β-hydroxyethyl)-benzaldehyde by reaction with terephthalic acid dichloride[52].

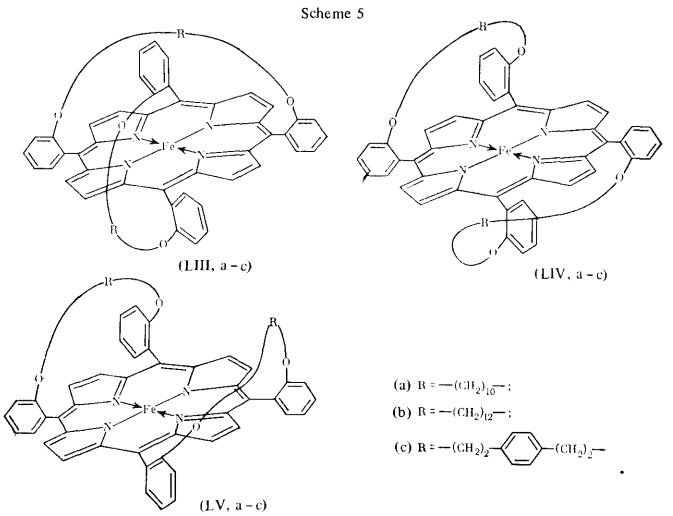
Scheme 4



The acid condensation of 1,10-di(2′-formylphenoxy)decane, 1,12-di(2′-formylphenoxy)dodecane, and 1,4-di[γ-(2′-formylphenoxy)propyl]benzene with pyrrole by the method of Kim et al.[54] yielded porphyrins of the "basket handle" type[55]. The three isomers (LIII), (LIV), and (LV) with crossing *trans*-binding, adjacent *trans*-binding, and adjacent *cis*-binding respectively, have been isolated by preparative chromatography (Scheme 5).

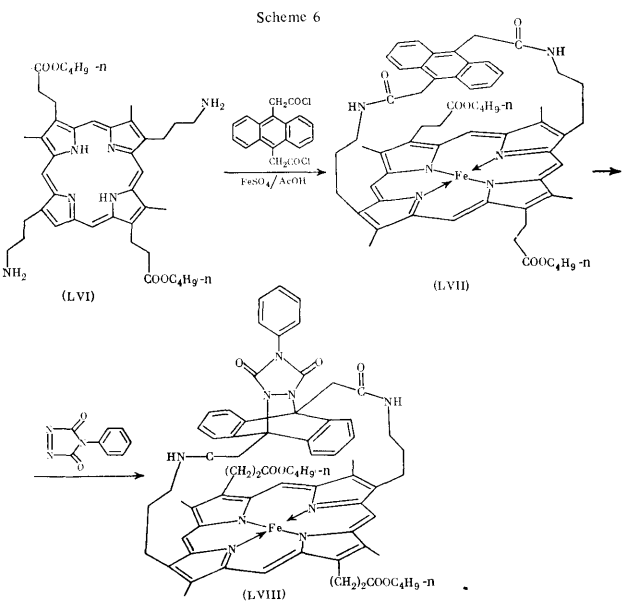
If the solution contains *N*-methylimidazole, then the iron(II) complexes of compounds (LIII), (LIV), and (LV) initially combine with two *N*-methylimidazole molecules, forming hexacoordinate complexes. The formation of these complexes with the isomers (LIII, a–c) requires a large excess of *N*-methylimidazole, apparently due to steric hindrance. When atmospheric oxygen is passed into a solution containing these complexes, one of the ligands (*N*-methylimidazole) is displaced by the oxygen. The oxygenating complexes formed are extremely stable[55].

Scheme 5



In order to increase the steric effects of the "distal" side of compounds modelling haemoglobin and myoglobin, the cyclophane porphyrins (LVII) and (LVIII) have been obtained[56] (Scheme 6).

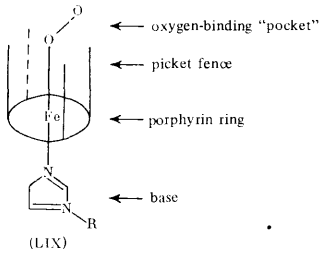
Scheme 6



The model compound (LVII) has been synthesised by the reaction of the diamino-derivative of the porphyrin (LVI) with the dichloride of anthracene-9,10-dicarboxylic acid[57]. The effect of the steric shielding of the "distal" side of the

model compound (LVIII) has been enhanced by the Diels–Alder reaction of the model compound (LVII) with 1-phenyltriazine-2,5-dione.

New sterically hindered porphyrins of the so-called "picket fence" type (LIX) have been synthesised[58–68]:



The acid condensation of *o*-nitrobenzaldehyde and pyrrole followed by the reduction of the product yielded *meso*-tetra-(*o*-aminophenyl)porphyrin (LX), which is a mixture of four atropisomers[59]. All the isomers have been isolated by preparative chromatography and have been identified on the basis of the results of Gottwald and Ullman[69] as the α,β,α,β-atropisomer (LXI), the α,α,β,β-atropisomer (LXII), the α,α,α,β-atropisomer (LXIII) and the α,α,α,α-atropisomer (LXIV).

The tetra-amides (LXV)–(LXVIII) have been synthsised by the reaction of *meso*-tetra-α,α,α,α-(*o*-aminophenyl)porphyrin with the chlorides of isophthalic, trimethylacetic, toluene-*p*-sulphonic, and nicotinic acids[58] (Scheme 7).

The interaction of compound (LXIV) with a limited amount of the chloride of trimethylacetic acid resulted in the formation of *meso*-tri-α,α,α-(*o*-pivalamidophenyl)-β-(*o*-aminophenyl)porphyrin (LXIX). Treatment of compound (LXIX) with 4-(*N*-imidazolyl)butyl chloride and 5-(*N*-imidazolyl)-penyl chloride led to the formation of the amides (LXX) and (LXXI) respectively[68] (Scheme 8).

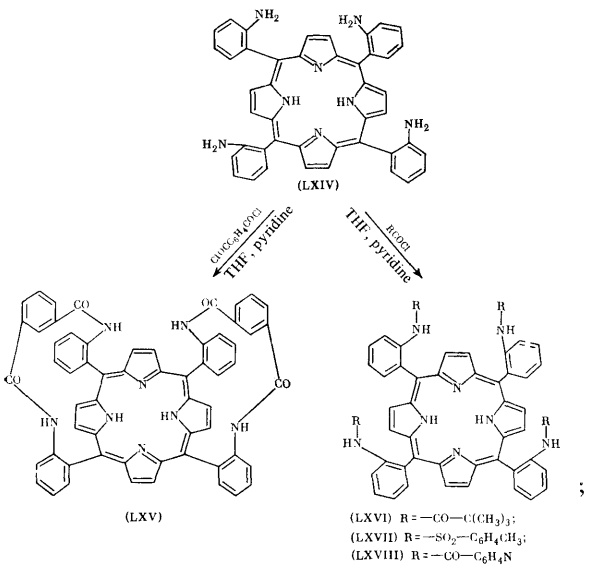
The iron(II) complexes of compounds (LXV)–(LXVIII), (LXX) and (LXXI) have been obtained by reducing the corresponding iron(III) complexes with chromium acetylacetonate. Their pentacoordinate and hexacoordinate compounds with axial ligands have also been obtained. After isolation, the crystalline oxygenating complexes of compounds (LXVI), (LXX), and (LXXI) are stable for a long time both in the solid state and in solution[58,68].

The iron(II) complexes of compounds (LXX) and (LXXI), in which one of the substituents is a base, namely 4-(*N*-imidazolyl)butyl or 5-(*N*-imidazolyl)pentyl, are of special interest. The length and conformation of this substituent can be controlled, which has a significant influence on the oxygen affinity.

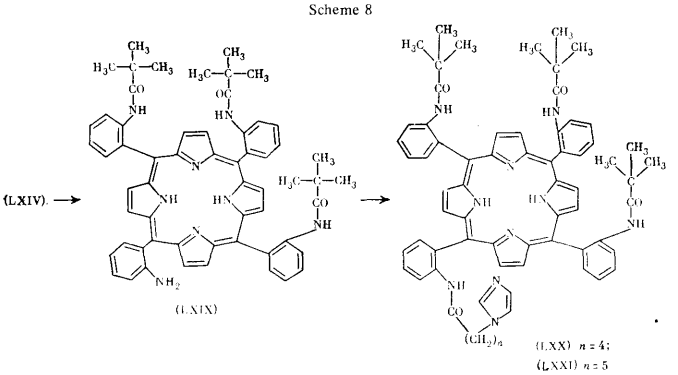
Bogatskii et al.[70] synthesised the "picket fence" and "belted" porphyrins (LXXII) and (LXXIII).

The steric shielding of one side of the porphyrin ring in the model compounds *meso*-tetra-α,α,α,α-(*o*-adamantamidophenyl)porphyrin (LXXIIa), *meso*-tetra-α,α,α,α-[*o*-3,4,5-trimethoxybenzamido)phenyl]porphyrin (LXXIIb), *meso*-tetra-α,α,α,α-(*o*-trimethylacetoamidophenyl)porphyrin (LXXIIc),[58] *meso*-tetra-α,α,α,α-(*o*-aminoacetamidophenyl)porphyrin (LXXIId), and *meso*-tetra-α,α,α,α-(*o*-acetamidophenyl)-porphyrin (LXXII) has been achieved using acid residues of different bulk (Scheme 9).

Scheme 7

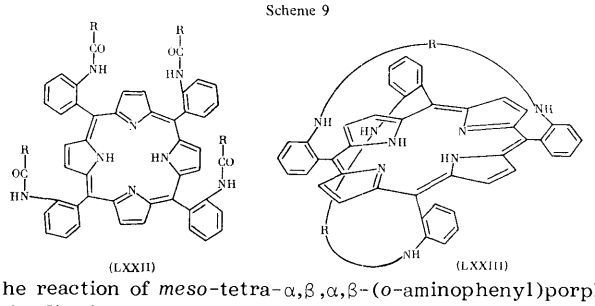


Scheme 8



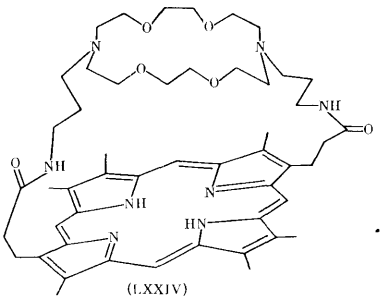
The tetra-amides (LXXII, a–e), where R = adamantyl for (a), R = 3,4,5-$(CH_3O)_3C_6H_2$ for (b), R = $C(CH_3)_3$ for (c), R = CH_2NH_2 or $-COCH_2OCH_2CH_2OCH_2CO-$ for (d), and R = CH_3 for (e), have been obtained by the reaction of *meso*-tetra-α,α,α,α-(*o*-aminophenyl)porphyrin (LXIV) [58] with the chlorides of adamantanecarboxylic, 3,4,5-trimethoxybenzoic, acetic, aminoacetic, and trimethylacetic acids in a THF–pyridine mixture at room temperature.

Scheme 9



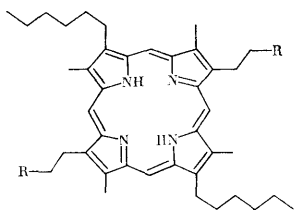
The reaction of *meso*-tetra-α,β,α,β-(*o*-aminophenyl)porphyrin (LXI) with the acid dichloride of triethyleneglycolic acid in a THF–pyridine mixture at a high dilution[43] yielded the cyclophane porphyrin (LXXIII) in which the two "bridges" form a belt around the porphyrin on either side. These porphyrins also form complexes capable of reversible oxygenation.

The crown-porphyrin (LXXIV) was obtained by Chang[57]. This dinuclear ligand permits the subsequent synthesis of composite complexes with both identical and different metals.



(LXXIV)

Dihexyldeuteroporphyrin (LXXVb) was chosen as the initial porphyrin for the synthesis of compound (LXXIV) because of its high solubility in organic solvents, which is very important for the successful separation and purification of the final bicyclic products from the starting material.

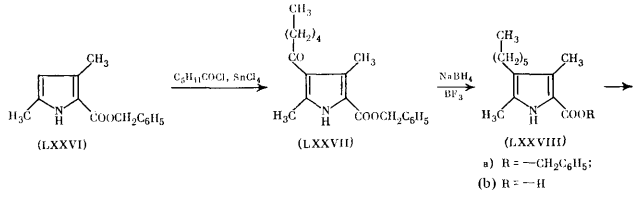


(LXXV)

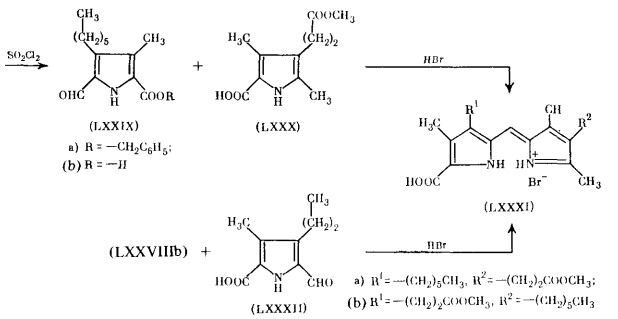
(a) R = —$COOCH_3$;
(b) R = —COOH;
(c) R = —COCl;
(d) R = —$CH_2OSO_2CH_3$;
(e) R = —$CH_2NH(CH_2)_3CH_3$;
(f) R = —$CH_2NHCH_2C_6H_5$

The hexyl side chains were introduced into the pyrrole components by acylating the pyrrole (LXXVI) in the presence of tin(IV) chloride with subsequent reduction of the resulting pyrrole (LXXVII).[71] Treatment of the pyrrole (LXXVIII) with sulphuryl chloride at high dilution yielded[72] the pyrrolealdehyde (LXXIX). After catalytic debenzylation, the free acid (LXXIXb) was mixed with an equimolar amount of the acid (LXXX)[73] and was treated with 48% hydrobromic acid at the boiling point. The pyrromethene (LXXXI) was formed instantaneously. After the removal of the solvent, the pyrromethene was subjected to self-condensation in hot formic acid in the presence of an excess of bromine, which resulted in the formation of the porphyrin (LXXVa); the latter can also be obtained in a high yield by condensing the pyrrole (LXXVIIIb) and the pyrrolealdehyde (LXXXII) via the intermediate dipyrromethene (LXXXI)[57] (Scheme 10).

Scheme 10



(LXXVI) (LXXVII) (LXXVIII)
a) R = —$CH_2C_6H_5$;
(b) R = —H

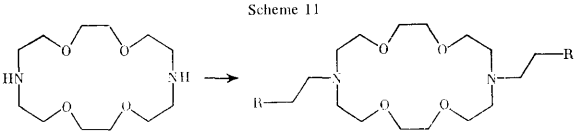


(LXXIX) (LXXX) (LXXXI)
a) R = —$CH_2C_6H_5$;
(b) R = —H

(LXXVIIIb) + (LXXXII)
a) R^1 = —$(CH_2)_5CH_3$, R^2 = —$(CH_2)_2COOCH_3$;
(b) R^1 = —$(CH_2)_2COOCH_3$, R^2 = —$(CH_2)_5CH_3$

The crown-ether component was synthesised from diaza-18-crown-6 derivative (LXXXIII).[74] The cyanoacetylene side chains were introduced by stirring the initial compound (LXXXIII) in acrylonitrile for 72 h. The diaminopropyl derivative of compound (LXXXIV) was obtained by reducing the cyano-group of compound (LXXXIV) in the presence of Raney nickel in a methanol solution of ammonia. The two ligands were coupled under the conditions of high dilution[57]. Compounds (LXXXVc) and (LXXXIVb) were poured simultaneously into a stirred 1 : 1 benzene–methylene chloride mixture over a period of 4 h. The crown-porphyrin (LXXIV) was isolated by column chromatography (Scheme 11):

Scheme 11



(LXXXIII) (LXXXIV) a) R = —CN;
(b) R = —CH_2NH_2

In the presence of *N*-methylimidazole and *N*-isobutylimidazole the iron(II) complex of the model compound (LXXIV) gives rise to a visible absorption spectrum typical for a hexacoordinate haemochrome compound. For a larger ligand, such as 1-triphenylmethylimidazole, the visible spectrum differs appreciably from the haemochrome spectrum; the oxygen-saturated specimen is stable at 25 °C for 1 h.[57]

III. PORPHYRIN DIMERS AND TRIMERS

Dimeric porphyrins of the "face-to-face" type (LXXXVII) and (LXXXIX) were first obtained by Collman et al.[75] Condensation of pyrrole (2 equivalents) with benzaldehyde (1 equivalent) and 2-nitrobenzaldehyde (1 equivalent) yielded a mixture of mono-di-, tri-, and tetra-(o-nitrophenyl)-porphyrin isomers and atropisomers. The reduction of the mixture of dinitroporphyrins, isolated by preparative chromatography, with tin(II) chloride led to a mixture of diaminoporphyrins, whose separation yields the α,α-*cis*-diaminoporphyrin (LXXXV)† and the *trans*-isomer (LXXXVIII).

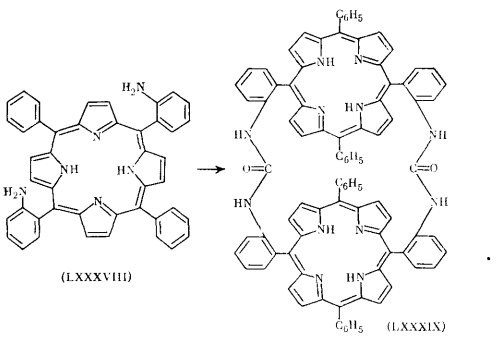
A solution of the diaminoporphyrin isomer (LXXXV) in benzene containing traces of pyridine was treated with phosgene and the excess phosgene was then removed. The

†The symbols α and β denote the opposite surfaces of the porphyrin plane; the *cis*- and *trans*-positions denote the adjoining and opposite *meso*-positions in tetraphenylporphyrins. Thus compound (LXXXV) is called 5-α-10-α-di(2-aminophenyl)-15,20-diphenylporphyrin or α,α-*cis*-diaminoporphyrin.

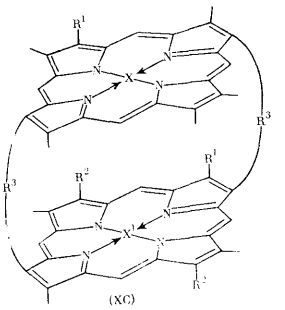
resulting solution was treated with an equivalent amount of a benzene solution of compound (LXXXV) (in nitrogen at 25 °C). Two diporphyrins, (LXXXVI) and (LXXXVII), linked by two urea "bridges", were obtained in this way. The porphyrin rings in the diporphyrin (LXXXVI) are located on different sides relative to one another, while in compound (LXXXVII) the porphyrin rings are arranged one above the other (Scheme 12). When α,α-*trans*-diaminoporphyrin (LXXXVIII) is used as the starting compound, only a single diporphyrin (LXXXIX) is formed. Two of the binary porphyrins (LXXXVII) and (LXXXIX) obtained are in the "face-to-face" conformation. The distance between the porphyrin rings in the copper and cobalt complexes of these compounds is approximately 6.5–6.8 Å.[75]

Diporphyrins of type (XC) [76–78] have been obtained similarly to compound (LXXIV), by the gradual introduction of equimolar amounts of the diamino-derivatives (LXXV, e and f) and the acid dichloride (LXXVc) in a methylene chloride–benzene mixture. The diporphyrin (XC) exists in the *syn*- and *anti*-isomeric forms; attempts to separate them by thin-layer chromatography were unsuccessful[76] (Scheme 13).

The dinuclear bimetallic complexes (XCc), (XCd), and (XCe), containing two identical metal atoms, have been obtained by a standard method[79]. The diporphyrin complex (XCf), containing only one copper atom, has been obtained[76] by the reaction of the copper complex (LXXVe) with the acid dichloride (LXXVc). The bimetallic complex (XCg) has been synthesised by introducing iron into the monometallic complex (XCf).[79]

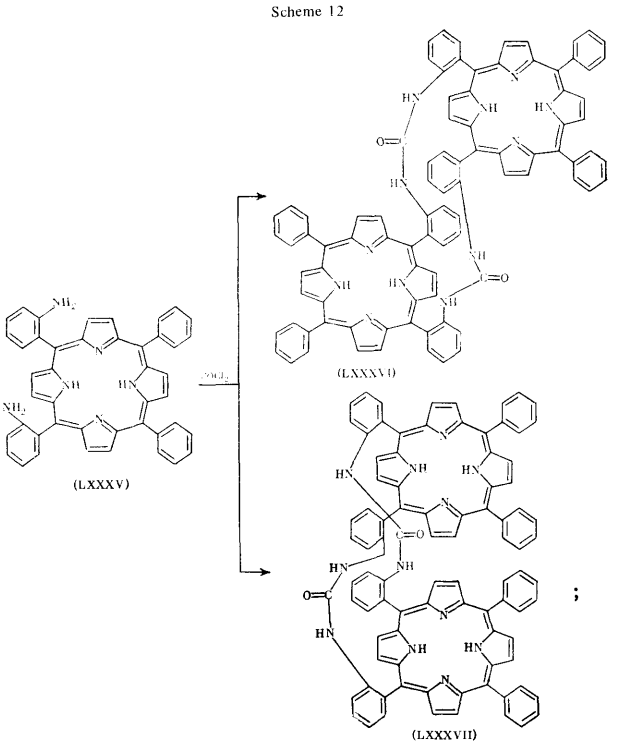


Scheme 13



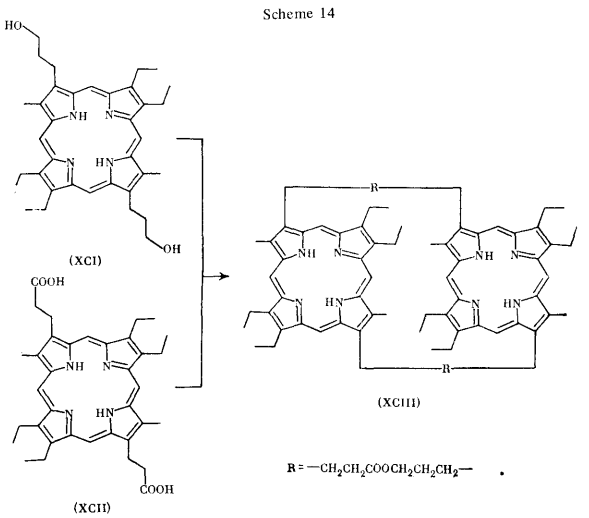
(a) $R^1=R^2=-(CH_2)_5CH_3$, $R^3=-(CH_2)_2CON(n\text{-}C_4H_9)(CH_2)_3$, $X=X^1=2H$;
(b) $R^1=R^2=-(CH_2)_5CH_3$, $R^3=-(CH_2)_2CON(CH_2C_6H_5)(CH_2)_3$, $X=X^1=2H$;
(c) $R^1=R^2=-(CH_2)_5CH_3$, $R^3=-(CH_2)_2CON(n\text{-}C_4H_9)(CH_2)_3$, $X=X^1=Fe^{III}Cl$;
(d) $R^1=R^2=-(CH_2)_5CH_3$, $R^3=-(CH_2)_2CON(n\text{-}C_4H_9)(CH_2)_3$, $X=Cu$, $X^1=Fe^{III}Cl$;
(e) $R^1=R^2=-(CH_2)_5CH_3$, $R^3=-(CH_2)_2CON(n\text{-}C_4H_9)(CH_2)_3$, $X=X^1=Zn$;
(f) $R^1=R^2=-(CH_2)_5CH_3$, $R^3=-(CH_2)_2CON(n\text{-}C_4H_9)(CH_2)_3$, $X=2H$, $X^1=Cu$;
(g) $R^1=R^2=-(CH_2)_5CH_3$, $R^3=-(CH_2)_2CON(n\text{-}C_4H_9)(CH_2)_3$, $X=Fe^{III}Cl$, $X^1=Cu$.

Scheme 12



The dimeric porphyrin (XCIII),[80] in which the two porphyrin rings are joined together by an ester fragment, has been obtained by treating a solution of the 3-hydroxypropyl derivative (XCI) and the carboxyethyl derivative (XCII) with isobutyl chloroformate in THF (Scheme 14). The attempt to separate the diester (XCIII) into the *syn*- and *anti*-isomers was unsuccessful, as before.

Scheme 14

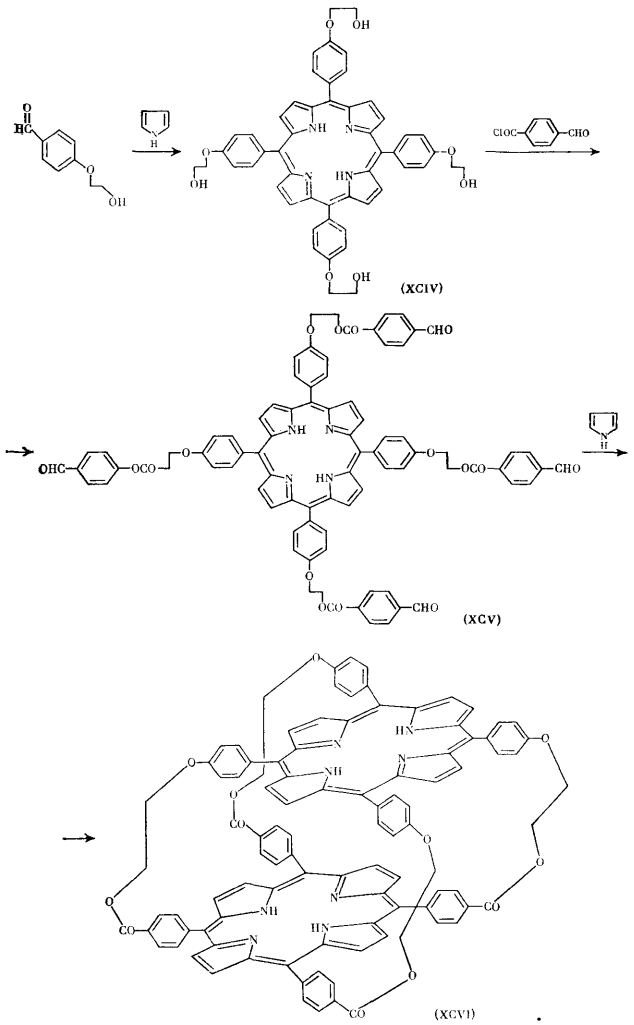


$R=-CH_2CH_2COOCH_2CH_2CH_2-$.

Treatment of the dimeric porphyrin (XCIII) with zinc acetate yielded[79] the corresponding bimetallic complex, for which the distance between the porphyrin rings was calculated and proved to be approximately 7 Å.

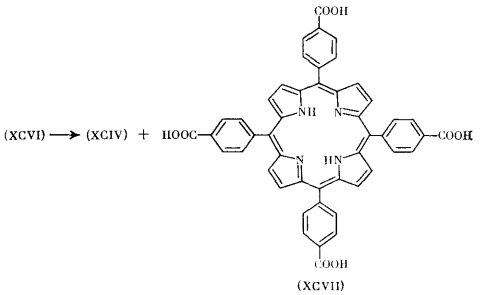
A layer (strati) diporphyrin (XCVI) has been obtained[81] by condensing the modified tetra-aldehyde (XCV) with pyrrole by the method of Adler et al.[82] The tetra-aldehyde (XCV) was obtained by the reaction of tetrahydroxyporphyrin (XCIV) with formylbenzoyl chloride[37] (Scheme 15).

Scheme 15



The structure of compound (XCVI) was proved[81] by identifying the products of its acid hydrolysis. Hydrolysis yielded only two products—compound (XCIV) and tetracarboxyporphyrin (XCVII) (Scheme 16).

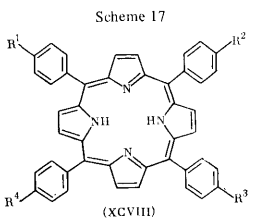
Scheme 16



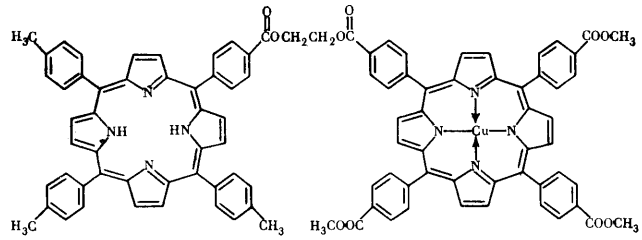
The synthesis of covalently linked porphyrins—the dimer (XCIX) and the trimers (C) and (CI)—has been achieved[83–85] and the transfer of the energy of the excited states between the two centres of the porphyrins has been investigated.

Transesterification of the tetramethyl ester (XCVIIIa) with ethylene glycol[84] leads to five isomers (XCVIII, b–f) after chromatographic separation. The condensation of 0.5 mole of *p*-toluic aldehyde, 0.1 mole of *p*-carboxybenzaldehyde, and 0.6 mole of pyrrole yielded a mixture of substituted *meso*-tetraphenylporphyrins, from which compound (XCVIIg) was isolated chromatographically[84]. The dimer (XCIX) has been obtained by the reaction of the acid chloride (XCVIIIh), synthesised by treating the corresponding acid (XCVIIIg) with oxalyl chloride, with the copper complex of 5-[4-(2-hydroxyethoxy)carbonylphenyl]-10,15,20-tri(4-methoxycarbonylphenyl)porphyrin[83]. The trimers (C) and (CI) have been obtained analogously from the copper complexes of substituted *meso*-tetraphenylporphyrins (XCVIIIc) and (XCVIIIf) respectively and the acid chloride (XCVIIIh) [84,85] (Scheme 17).

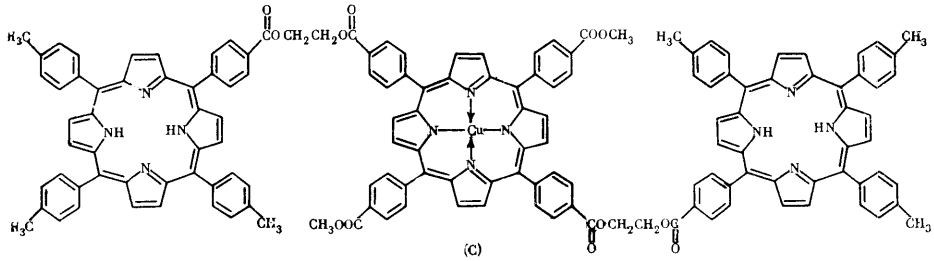
Scheme 17



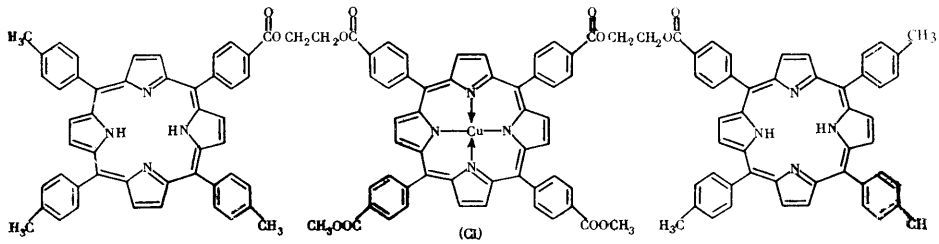
(a) $R^1=R^2=R^3=R^4=-COOCH_3$;
(b) $R^1=-COOCH_2CH_2OH$, $R^2=R^3=R^4=-COOCH_3$;
(c) $R^1=R^3=-COOCH_2CH_2OH$, $R^2=R^4=-COOCH_3$;
(d) $R^1=R^2=R^3=-COOCH_2CH_2OH$, $R^4=-COOCH_3$;
(e) $R^1=R^2=R^3=R^4=-COOCH_2CH_2OH$;
(f) $R^1=R^2=-COOCH_2CH_2OH$, $R^3=R^4=-COOCH_3$;
(g) $R^1=-COOH$, $R^2=R^3=R^4=-CH_3$;
(h) $R^1=-COCl$, $R^2=R^3=R^4=-CH_3$



(XCIX)

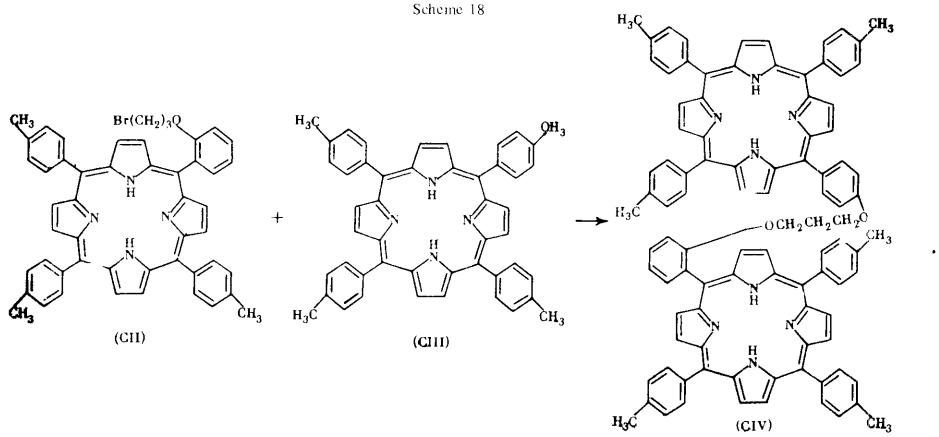


(C)



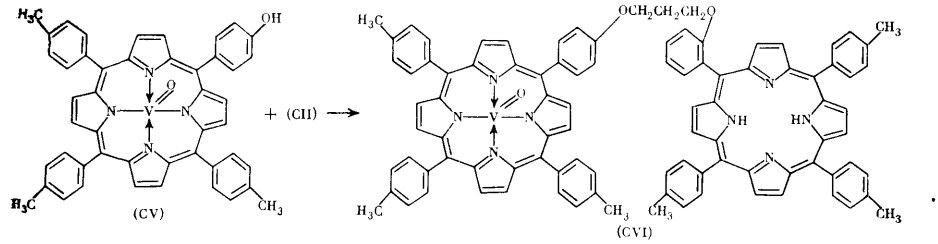
(CI)

Scheme 18



(CII) (CIII) (CIV)

Scheme 19



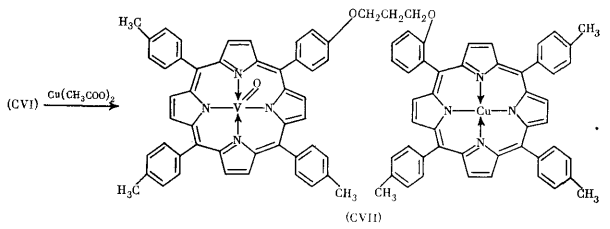
(CV) (CVI)

The covalently linked dimer (CIV) has been obtained[86] by the reaction of 5-[*o*-(3-bromopropoxy)phenyl]-10,15,20-tritolylphenylporphyrin (CII) with one equivalent of 5-(*p*-hydroxyphenyl)-10,15,20-tritolylphenylporphyrin (CIII) [87] (Scheme 18).

Vanadylporphyrin (CV), obtained by the usual methods[51,88], readily reacts with the porphyrin (CI) to form the vanadium-containing dimer (CVI) (Scheme 19).

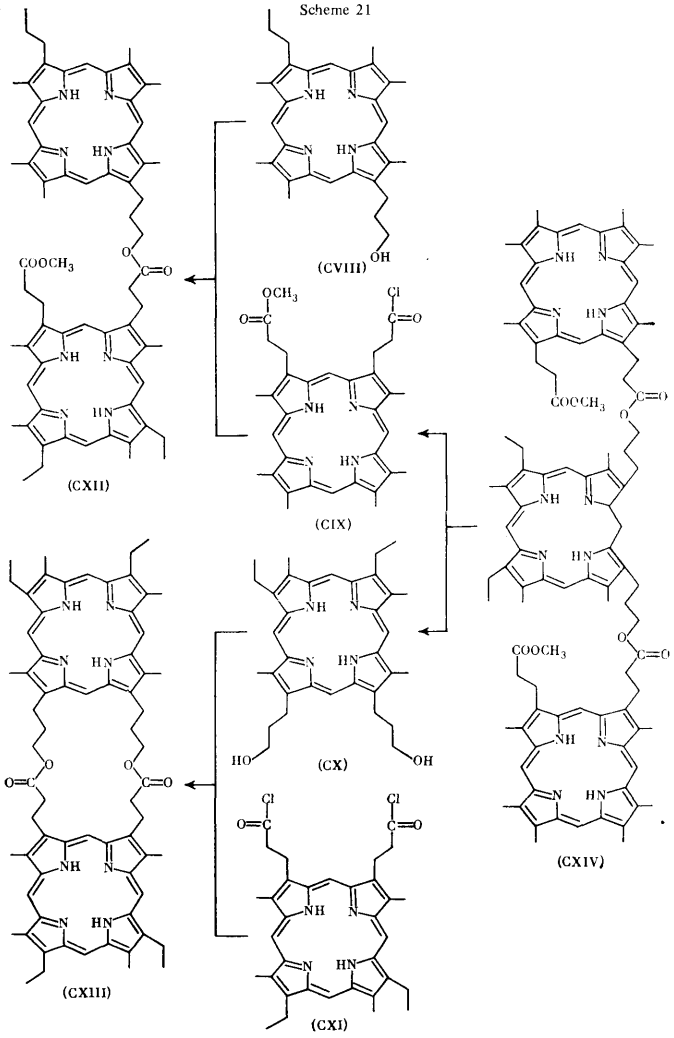
The mixed copper–vanadium complex (CVII) can be synthesised by Falk's method[51] involving the treatment of compound (CVI) with copper acetate in pyridine (Scheme 20).

Scheme 20



Japanese investigators[89,90] obtained the covalently linked dimers (CXII) and (CXIII) and the trimer (CXIV) of natural porphyrins (Scheme 21).

Scheme 21

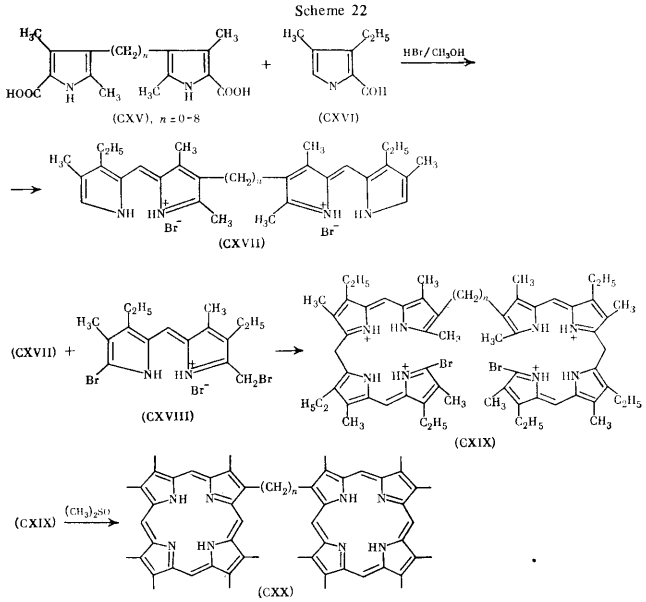


2-(2-Ethoxycarbonylethyl)-3,7,8,17,18-hexamethyl-12-propylporphyrin has been synthesised by Johnson's method[91] and then converted by hydrolysis into the acid; reduction of the latter[92] leads to the 3-hydroxypropyl derivative (CVIII). The dimethyl ester of mesoporphyrin-IX has been converted by partial hydrolysis into a mixture of two isomers of the monomethyl ester of mesoporphyrin-IX and then into the acid chloride (CIX) by treatment with thionyl chloride. Reduction of the dimethyl ester of mesoporphyrin-IX yielded di(3-hydroxypropyl)porphyrin (CX), [92] while treatment with thionyl chloride afforded the dichloride (CXI).

The covalently linked dimer (CXII) has been obtained by the reaction of the 3-hydroxypropyl derivative of the porphyrin (CVIII) with the acid chloride (CIX) in methylene chloride in the presence of triethylamine at a high dilution. The diporphyrin (CXIII) has been obtained analogously from the dihydroxy-derivative (CX) and the acid dichloride (CXI), while the trimer (CXIV) has been synthesised from two moles of the acid chloride (CIX) and one mole of the dihydroxy-derivative (CX). [89]

The covalently linked diporphyrin (CXX) has been obtained[93] from the dipyrrole (CXV). Condensation of the dipyrroles (CXV) with 2-formylpyrrole (CXVI) in a mixture of acetic and hydrobromic acids yielded the corresponding dihydrobromides of bisdipyrrolylmethenes (CXXII), from which the bisporphyrins (CXX) were obtained by reaction with the hydrobromide of the bromo-derivative of dipyrrolylmethene (CXVIII) and the Johnson cyclisation[91] of the intermediate bisbiladienes (CXIX) [93] (Scheme 22).

Scheme 22

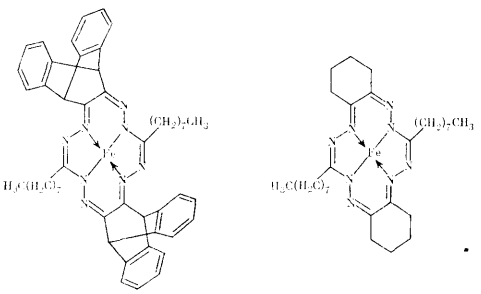


IV. CONCLUSION

The data presented show that in recent years there has been a rapid development of the research into the synthesis of sterically hindered porphyrins. Attention has been concentrated on the preparation of stereochemical models of the "hydrophobic pocket", the size of which has been estimated as 5.6–6.0 Å.

In this connection attempts have been made at a wider employment of the ideas of such modelling. Thus Baldwin and Huff[94] proposed models of the tetra-aza-compounds (CXXI) and (CXXII), which are not porphyrins but have

"hydrophobic pockets" of different depth, in order to demonstrate the validity of the approach under discussion. Baldwin showed that compound (CXXI), which has a 5.0 Å "hydrophobic pocket", is capable of reversible oxygenation, while the related compound (CXXII), where the "pocket" is less deep (~2.2 Å) is incapable of such oxygenation:



(CXXI) (CXXII)

We believe that the study of Baldwin and Huff[94] is extremely important, since it demonstrates the universality of the stereochemical approach to the problem of the reversible oxygenation and leads to extensive possibilities for molecular design in this field. The creation of stereochemical models of this kind on the basis of different macrocyclic tetra-aza-compounds might give rise to a new additional field of research in the synthesis of effective oxygen transferring agents.

Further development of studies on the synthesis of new models of sterically hindered porphyrins and the investigation of their properties appear to be exceptionally important both for physicochemical biology and for catalysis, the chemistry of biologically active substances, and the chemistry of medicinal preparations. It may be hoped that compounds effectively modelling not only the work of haemoglobin but also that of chlorophyll will be synthesised in the immediate future.

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Surface and Porosity of Adsorbents

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The validity of adsorption methods of measuring specific surface areas of solids (and, in particular, of adsorbents) is limited by the characteristics of the porosity. Methods based on the concept of multilayer adsorption, like the BET method and de Boer's *t*-method, are applicable only to non-porous or coarsely porous (including mesoporous) adsorbents.
There is no general method of calculating the surface area of microporous adsorbents from adsorption data. For the "crack" model of the micropores in carbon adsorbents we can calculate the size and the geometrical area of the micropores from the parameters of the adsorption equation given by the theory of the volume filling of micropores, using a standard vapour (benzene). Almost identical results are obtained by using the adsorption of water vapour, which forms continuous monolayers in the micropores because of the dominant role of the hydrogen bond in adsorption. The geometric surface of micropores in carbon adsorbents is not a measure of the adsorption capacity of the sample, which is determined by dispersion forces, but it is relevant in kinetics and catalysis.
The presence of micropores in non-porous or coarsely porous adsorbents makes the measurement of surface area by the BET or the de Boer method physically meaningless. In this case we can use the t/F method of Dubinin and Kadlets, which gives a measure of the volume of micropores and of the specific surface of mesopores. Kistler and Kiselev's capillary condensation method gives similar values for the specific area of the mesopores. 23 References.

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I. INTRODUCTION

The two extreme cases of physisorption are adsorption on non-porous adsorbents and adsorption in the finest pores (the micropores). The porosity of adsorbents is one of the main factors in adsorption. On the basis of adsorption and capillary phenomena pores can be conveniently classified according to their linear size x into micropores (x < 0.6 to 0.7 nm), supermicropores (0.6–0.7 < x < 1.5–1.6 nm), mesopores (1.5–1.6 < x < 100–200 nm), and macropores (x > 100–200 nm).[1] The smallest pores in adsorbents (the micropores) are comparable in size with adsorbed molecules. As a result of the superposition of the fields of dispersion forces from opposite walls of the micropores, adsorption energies in micropores are relatively high. As an example, we show in Fig.1 the dependence of the differential heat of adsorption of benzene on an activated and on a non-porous carbon adsorbent (gas carbon heated *in vacuo* at 950 °C) on the relative adsorption $\theta = a/a_{0.2}$.[2] This large difference in adsorption energy is the fundamental reason for the

difference between adsorption in micropores and adsorption on a non-porous carbon adsorbent. Adsorption in micropores is characterised by volume filling of the adsorption space of the micropores, i.e. of the adsorption field of force.

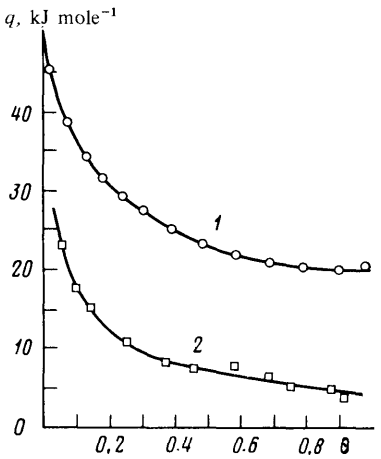


Figure 1. Differential heats of adsorption of benzene (q) for active carbon (*1*) and for "950 carbon" (*2*).[13]

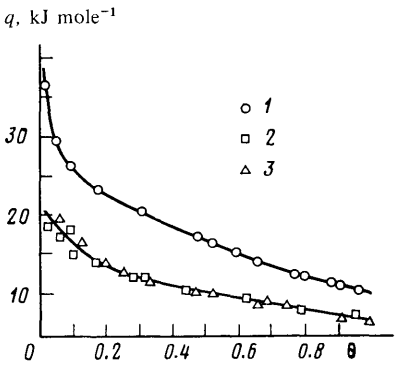


Figure 2. Differential heats of adsorption of benzene for supermicroporous (*1*) and non-porous (*2*, *3*) silicas[13].

Adsorption in mesopores, like adsorption on non-porous adsorbent surfaces, leads to the formation of successive adsorbed layers on the mesopore walls, and ultimately results in filling of the mesopores by the capillary condensation mechanism. Supermicropores occupy a porosity region intermediate between those of micropores and mesopores, in which the properties of micropores gradually disappear and those of mesopores become evident. We note from Fig. 2 that the adsorption energy is increased also in the supermicropores of silica adsorbents, but the effect is less marked than in micropores.

Pores having a diameter greater than 100–200 nm cannot be filled by capillary condensation in practice, and therefore they are usually treated as a form of macropore. Macropores (and, in many cases, mesopores) act as transport pores in adsorption. On the other hand, micropores and supermicropores determine the capacity of the adsorbent towards gases and vapours, and therefore they are called adsorption pores.

The linear dimensions of zeolite holes, usually less than 0.5–0.6 nm, are typical of micropores. Their adsorption space contains cations whose charge is compensated by the excess of negative charge in the alumino-silicate skeleton. The cations behave as active centres, giving a locally enhanced electrostatic interaction (especially for the adsorption of polar molecules). Therefore in many cases the adsorption energy in zeolites is greater than in microporous carbon adsorbents, i.e. the adsorption capacity of the zeolites is greater, especially towards adsorbates having a low equilibrium pressure. The mesopores in formed zeolites are the gaps between adjacent crystallites, held together by the binder.

II. SPECIFIC SURFACE OF NON-POROUS AND OF RELATIVELY COARSELY POROUS ADSORBENTS

In mesoporous (and even more so in macroporous) adsorbents the effect of surface curvature on adsorption is negligible. Therefore we can assume that the adsorption of gases and vapours per unit surface area occurs by the same mechanism in non-porous, macroporous, and mesoporous adsorbents of the same chemical type.

A general theory of physisorption of gases and vapours on non-porous adsorbents has not yet been developed. The Brunauer, Emmett, and Teller (BET) multimolecular vapour adsorption theory[3] is applicable only over a narrow range of equilibrium relative pressures: for example, 0.05–0.35 for the low-temperature adsorption of nitrogen. Therefore the BET isotherm equation is more useful for calculating (from one of its parameters) the specific surface area than for describing the dependence of the physisorption of a vapour on its equilibrium relative pressure. The equation is usually written

$$a = a_m ch/(1-h)[1+(c-1)h] ,$$

where a is the adsorption at the equilibrium relative pressure p/p_s, and $h = p/p_s$. The parameters of the equation are the adsorption a_m, corresponding to the formation of a monolayer of adsorbed molecules (the monolayer capacity), and the constant c, related to the adsorption energy. These parameters are easily determined graphically by linearising the equation. If ω is the area occupied by one molecule in the filled monolayer (the molecular area), and the monolayer capacity a_m is given in mmole g^{-1}, the surface area per unit mass of adsorbent (or specific surface) S can be written

$$S = a_m \omega N , \qquad (1)$$

where $N = 6.02 \times 10^{20}$ is the number of molecules in 1 mmole of adsorbate.

The standard adsorbate usually chosen for measuring specific surfaces of adsorbents is nitrogen at its boiling point (78 K) and atmospheric pressure: its molecular area ($\omega = 0.162$ nm^2 or 16.2 Å^2) is calculated from the density of liquid nitrogen. This molecular area gives the best agreement with measurements of the specific area of porous solids by other methods (for example, by electron microscopy). However, if molecular areas calculated in the same

way for other vapours are used, significant deviations in the BET specific surface areas are obtained. Table 1 (from Ref.4) lists ω values and the corresponding ratios of the specific surface obtained experimentally to the surface obtained with nitrogen, S/S_{N_2}. We note that the deviation can be as high as 34%. The BET method is basically empirical, and it can be used to measure the specific surface of non-porous or coarsely porous adsorbents by the low-temperature adsorption of nitrogen to a precision of ~15–20%.

The reduced adsorption isotherm method[5] is far simpler to use in estimating specific surfaces of non-porous or coarsely porous adsorbents.

Table 1.

Vapour	T, K	ω, nm^2	S/S_{N_2}
Nitrogen	78	0.162	1.00
Krypton	78	0.152	0.73
n-Butane	273	0.321	0.68
Freon-21	273	0.204	0.66

The method is based on the isotherm equation for the adsorption of the experimental vapour on a non-porous adsorbent whose specific surface has been determined with nitrogen by the BET method. Calculation of the adsorption γ for unit surface of the adsorbent gives the adsorption isotherm

$$\gamma = f(h). \qquad (2)$$

For the coarsely porous adsorbent (with a chemically similar surface) whose specific surface area is required we can write the isotherm as

$$a = S\gamma = Sf(h). \qquad (3)$$

Eqns.(2) and (3) for each adsorbent can be displayed as tables of the parameters γ and a for identical equilibrium relative pressures, obtained by interpolation from plots of the experimental adsorption isotherms. According to Eqn.(3) the plot of $a = \psi(\gamma)$ is a straight line passing through the origin, with a slope numerically equal to the specific surface of the adsorbent. The reduced isotherm method is not limited by the nature of the adsorbed vapour: the only validity condition is chemical similarity between the two surfaces, which determines the similarity of the adsorption isotherms (2) and (3). A solution of the problem in the absence of similar isotherms has also been proposed[6].

The t-method (de Boer and Lippens[7]) is very similar to the above. The only difference is that in the analogue of Eqn.(3) adsorptions are expressed as the volume of liquid adsorbate V. Eqn.(3) then becomes

$$V = St = S\varphi(h), \qquad (4)$$

where t is the average thickness of the adsorbed layer of nitrogen. In this case an equation of the type of (2), i.e.

$$t = F(p/p_s),$$

expresses the dependence of the thickness of the adsorption layer on the relative pressure. This dependence is called the t-curve, and for nitrogen at 78 K it is summarised below[7]:

p/p_s	0.050	0.080	0.100	0.160	0.200	0.240	0.280	0.340	0.400	0.450
t, nm	0.321	0.348	0.359	0.401	0.428	0.455	0.486	0.533	0.575	0.607

By plotting, as above, V against t according to Eqn.(4) we obtain a straight line passing through the origin whose slope is numerically equal to the wanted specific surface. The t-method was proposed by de Boer and Lippens to study the low-temperature adsorption of nitrogen on alumina or silica minerals. The t-curves for these types of mineral are almost identical.

III. ADSORPTION IN MICROPORES AND GEOMETRIC SURFACE AREA OF MICROPOROUS ADSORBENTS

The effective increase in the heat of adsorption or adsorption potential in micropores radically changes the way in which the adsorption space is filled during adsorption in the case of micropores. The formation of successive adsorbed layers (on non-porous adsorbents) is replaced by the volume filling of the adsorption space, i.e. of the field of adsorption forces[8,9]. The writer's theory of adsorption in micropores[10–13], which has been called the theory of volume filling of micropores (TVFM), has been widely used, especially in systems involving microporous carbon adsorbents or active carbons.

The basic equation of this theory is

$$a = \frac{W_0}{v^*} \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right], \qquad (5)$$

where a is the adsorption at the equilibrium relative pressure p/p_S and temperature T, and A is the change in Gibbs free energy, taken with the negative sign and expressed as

$$A = RT \ln(p_s/p). \qquad (6)$$

Also, W_0 is the maximum volume of the adsorption space (or micropore volume), E_0 is the characteristic adsorption energy for the standard vapour, β is a similarity coefficient, defined in terms of physical constants of the experimental and the standard substance, and n is a parameter (integer). The molar volume (v^*) of the substance in the adsorbed state, i.e. of the adsorbate at unit relative pressure, is a function of temperature and can be calculated from the physical constants of the adsorbate or adsorband.

The TVFM adsorption equation (5) has three parameters: W_0, E_0, and n. For microporous adsorbents we usually have $n = 2$. In the case of the adsorption of gases or vapours on zeolites the integer n can take values between 2 and 6, depending on the size of the zeolite holes and on the density of active centres (i.e. cations) within the holes. An approximate estimate of n can be obtained from the TVFM equation (5) by taking logarithms twice (see Ref.13). Knowing n, we can determine W_0 and E_0 by plotting Eqn.(5) in a linearised form (taking logarithms of both sides).

Very many examples of the satisfactory application of the TVFM equation (5) to the adsorption of vapours on active carbons in temperature ranges over 100–150 K wide have been reported. Some examples of the application of the TVFM equation to zeolites are given below. A detailed discussion of the determination of the parameters of the equation is given in Ref.13.

1. Adsorption of methane on zeolite L between 156 and 243 K.[14] The parameters of Eqn.(5) at normal temperature and pressure, determined from the adsorption isotherm for 192 K, were: $W_0 = 46.8$ cm^3 g^{-1} and $E = 9.84$ J mole^{-1} (for CH_4) with $n = 3$. Experimental and calculated adsorption isotherms are compared in Fig.3.

2. Adsorption of carbon dioxide on K,Na-erionite at 293–413 K (from data obtained by Meerson and Stepanov, see Ref.13). The parameters of Eqn.(5) were determined

from the adsorption isotherm for 383 K: $W_0 = 12.4\%$, $E = 21.9$ kJ mole^{-1}, and $n = 3$. Calculated and experimental adsorption isotherms are shown in Fig. 4.[13] In both cases the agreement between calculation and experiment is satisfactory.

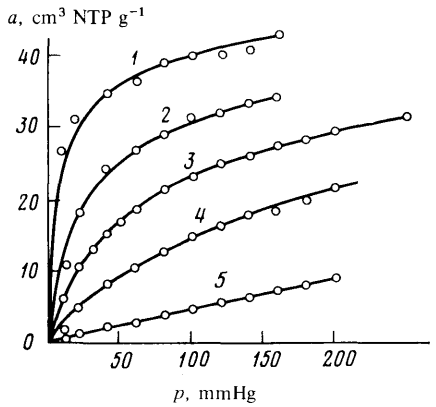


Figure 3. Calculated (curves) and experimental (points) isotherms for the adsorption of methane on zeolite L at: *1*) 156, *2*) 178, *3*) 193, *4*) 212, *5*) 243 K.[13]

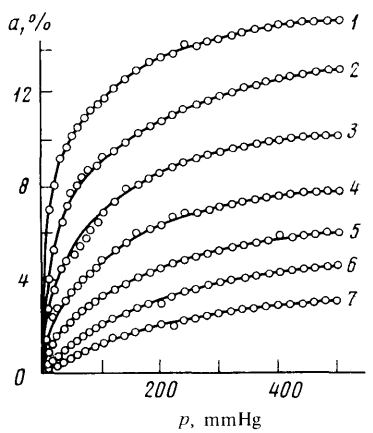


Figure 4. Calculated (curves) and experimental (points) isotherms for the adsorption of carbon dioxide on K,Na-erionite at: *1*) 293, *2*) 313, *3*) 333, *4*) 353, *5*) 373, *6*) 393, *7*) 413 K.[13]

It is interesting to compare the adsorption properties of natural clinoptilolite from the Dzegbi deposits with those of active carbon from coconut shells (combustion loss 50%) for CO_2 at 293 K and $n = 2$:[15]

Sorbent	Clinoptilolite	Carbon
W_0, cm³ g⁻¹	0.100	0.230
E, kJ mole⁻¹	28.5	10.3

In clinoptilolite the micropore volume is one-half that of active carbon, and the characteristic energy of adsorption of carbon dioxide is higher by a factor of 3. The adsorptions (a, mmole g^{-1}) of carbon dioxide on clinoptilolite and on active carbon at 293 K are compared in Table 2: at relatively low pressures (up to $p \approx 400$ mmHg) the adsorption on clinoptilolite is between 17 and 1.4 times greater than on active carbon in spite of the smaller (2.3-fold) adsorption volume in the zeolite than in the carbon. This is due to the higher characteristic energy of adsorption in the zeolite.

Table 2. Adsorption of carbon dioxide at 293 K.[15]

p/p_s	a, mmole g⁻¹	
	clinoptilolite	active carbon
$5\cdot10^{-5}$	1.26	0.075
$1\cdot10^{-4}$	1.46	0.12
$5\cdot10^{-4}$	1.61	0.29
$1\cdot10^{-3}$	1.72	0.49
$5\cdot10^{-3}$	1.99	1.38

Active carbons and zeolites are the most widely used microporous adsorbents. Their pores are the smallest of all adsorbents, comparable in size with adsorbed molecules. The volume of the micropores usually lies between 0.1 and 0.6 cm^3 g^{-1}. However, the micropore structure of zeolites (unlike that of active carbons) is due to the crystal structure of these materials and hence is strictly regular. This allows us to calculate with great precision the size, volume, and geometric surface of the micropores from X-ray diffraction data. Thus, for CaA zeolite crystals we found[16] a total volume of large holes $v = 0.278$ cm^3 g^{-1} and a geometric surface area of pore walls $S_g = 1640$ m^2 g^{-1}, and for NaX zeolite $v = 0.322$ cm^3 g^{-1} and $S_g = 1400$ m^2 g^{-1}.

However, in contrast to non-porous and coarsely porous adsorbents (for which the adsorption is directly proportional to the specific surface), in the case of volume filling of micropores the adsorption is not determined by the geometric surface of the micropores. The concept of a monolayer also becomes meaningless for adsorption in micropores. Formally, a "monolayer capacity" a_m can be obtained according to formula (1) if the geometric surface area of the pores is known. For a CaA zeolite with $S_g = 1640$ m^2 g^{-1} we obtained $a_m = 16.6$ mmole g^{-1} for the adsorption of nitrogen ($\omega = 0.162$ nm^2) at 78 K. Experimentally, the limiting adsorption of nitrogen on CaA zeolite for $h = 1$ is $a_0 = 8.27$ mmole g^{-1}, i.e. approximately one-half of the estimated monolayer capacity. We conclude that for zeolites the geometric specific surface cannot be determined from adsorption measurements.

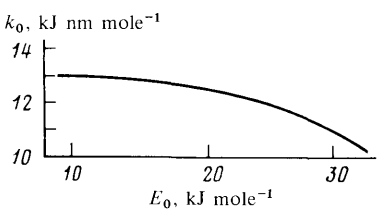


Figure 5. Dependence of the parameter k_0 on E_0.[19]

Unlike those of zeolites, the geometric surface areas of microporous carbons can be calculated and determined experimentally from adsorption data. According to

currently held views the micropores in carbon adsorbents resemble flat cracks, and their main parameter is the half-width x of the crack. We have used[17] X-ray diffraction and adsorption data to show that the half-width x of the micropores is inversely proportional to the characteristic adsorption energy of the standard vapour (benzene):

$$x = k_0/E_0, \quad (7)$$

where the parameter k_0 is only weakly dependent on E_0 (see Fig.5).[17,18].

Knowing the parameters of the TVFM equation (5) for $n = 2$, i.e. the micropore volume W_0 ($cm^3\ g^{-1}$) and the characteristic adsorption energy E_0 (kJ $mole^{-1}$), we can easily calculate by Eqn.(7) the half-width of the plane-parallel micropores (x, nm), and by using the elementary formula (8) we can arrive at the geometric surface of the micropore walls in active carbon[19]:

$$S_g,\ m^2\ g^{-1} = 10^3 W_0/x. \quad (8)$$

Unlike the adsorption of organic vapours on active carbons, in which the role of dispersion forces is predominant, the adsorption of water is controlled by hydrogen bonds both between the primary adsorption centres (oxygen surface compounds) and between the water molecules. In this case the dispersion interaction energies are weaker than the hydrogen bond energies and can be ignored. Since the interactions arising from hydrogen bonding are not amplified in the micropores the adsorption on micropore walls takes place by the same mechanism as on the surface of a non-porous carbon adsorbent (gas carbon heated at 950 °C in vacuum[19]).

Table 3. Specific surface areas ($m^2\ g^{-1}$) of model microporous carbon adsorbents (benzene, 293 K, $W_0 = 0.500\ cm^3\ g^{-1}$).[19]

E_0, kJ mole^{-1}	x, nm	S_g	S_{BET}	S_t
18.9	0.67	750	1200	1450
13.3	0.97	520	1170	1280
9.4	1.38	360	1040	1050

From the experimental results, an average monolayer of water molecules adsorbed on "950 °C" carbon black of known specific surface area is formed at an equilibrium relative pressure of water vapour $h = 0.60$ at 293 K. Taking the molecular area of water as $\omega = 0.105\ nm^2$ we conclude that 1 mmole of water in the form of a monolayer occupies an adsorbent surface $K = \omega N = 63.2\ m^2\ mmole^{-1}$. If the adsorption of water on an active carbon at $T = 293$ K and with $h = 0.6$ is $a_{0.6}$ mmole g^{-1}, the geometric surface of the pore walls can be expressed as[19]

$$S_g^{H_2O},\ m^2\ g^{-1} = Ka_{0.6} = 63.2a_{0.6}. \quad (9)$$

The geometric surface areas of micropores in different types of active carbon, obtained[19] from the adsorption isotherms of benzene and of water by using Eqns.(8) and (9) respectively, are compared below:

Active carbon	KL2	KL3	AG1	V3	KL4	EK3	V4	KL5	KL6
S_g	560	680	640	540	720	580	680	840	870
$S_g^{H_2O}$	610	620	740	660	710	690	730	880	990
$S_g^{H_2O}/S_g$	1.09	0.91	1.16	1.22	0.99	1.19	1.07	1.05	1.14

The discrepancies between the two sets of results are well within the uncertainty limits of different methods of measuring the surface area of adsorbents.

It may be useful also to compare different methods of calculating the surface area of micropores in order to assess their physical reality. In this analysis we used model adsorption isotherms for benzene, calculated by the TVFM equation for $n = 2$ and $W_0 = 0.50\ cm^3\ g^{-1}$ and for a range of E_0 values determined by low-angle X-ray diffraction measurements[19]. As we have already shown, the TVFM equation is satisfactorily consistent with experimental data. The adsorption isotherms obtained in this way were treated by the BET method and by the de Boer t-method. The geometric surface areas of micropores S_g were calculated by formula (8): the results are shown in Table 3.

Table 4. Specific surface areas ($m^2\ g^{-1}$) of industrial active carbons[9].

Active carbon	S_g	$S_g^{H_2O}$	S_{BET}
AG2	460	470	800
SKT	1350	1460	2160

The geometric surfaces S_g seem to give a realistic indication of the surface area of the walls of the plane-parallel micropores. Their physical reality is confirmed by two independent methods, whose results for water and benzene adsorption are mentioned above[19]. The BET and de Boer specific surfaces are mutually consistent, but far from compatible with real values. The results shown in Table 4 were obtained in a similar way for industrial active carbons from the experimental adsorption isotherms for benzene and water at 293 K. We again note the almost identical geometric surface areas for each type of carbon given by the adsorption isotherms for benzene and for water, and the large discrepancies with the S_{BET} values. Hence we conclude that the specific surface areas of microporous adsorbents based on the multilayer adsorption model, i.e. the values given by the BET and the de Boer t-method, are physically unjustifiable. On the other hand the geometric surfaces have a clear physical meaning. However, they are only relevent to the adsorption of water, and possibly of ammonia, whose isotherms on active carbons have similar shapes. The geometric surface area of micropores bears no relationship whatever to the adsorption characteristics of other vapours on active carbon.

Nevertheless, the geometric surface of micropores could be kinetically significant in the description of surface mass transfer processes and in catalysis, when the microporous carbon adsorbents are used as catalysts or as carriers of catalytically active additives.

IV. ADSORPTION IN MICROPORES AND MESOPORES

If the adsorbent contains micropores as well as mesopores we can expect adsorption on both types of pore under the conditions in which the t-method is applied. The total adsorption V (expressed as volume of liquid adsorbate) will include contributions from the adsorption in micropores (V^{mi}) and in mesopores (V^{me}). The adsorption on the surface of macropores is negligibly small and will be ignored in this analysis. Therefore we have

$$V = V^{mi} + S_{me}t, \quad (10)$$

where the product $S_{me}t$ gives the adsorption in mesopores. For equilibrium relative pressures in the range $h = 0.05-0.4$, for example in the case of the low-temperature adsorption of nitrogen, the changes in adsorption in the micropores (ΔV^{mi}) are comparable to the changes in adsorption in the mesopores. Therefore the dependence of the total adsorption on the thickness of the adsorption layer is not linear, and the t-method is not applicable.

According to the TVFM equation (5) the extent of filling of the micropore volume F for $n = 2$ can be expressed, in this case as

$$F = V^{mi}/W_0 = \exp[-(A/E)^2] ,$$

where E is the characteristic adsorption energy for the vapour being studied. Dividing both sides of Eqn.(10) by F gives

$$V/F = W_0 + S_{me}t/F . \qquad (11)$$

This is the basic equation of the Dubinin–Kadlets t/F method[20]. To a good approximation W_0 is equal to the volume of micropores ($v_{mi} = W_0$). In V/F against t/F coordinates Eqn.(11) gives a straight-line plot which intersects the vertical axis at v_{mi}. The slope of the straight line is a measure of the specific surface area of the mesopores S_{me}.

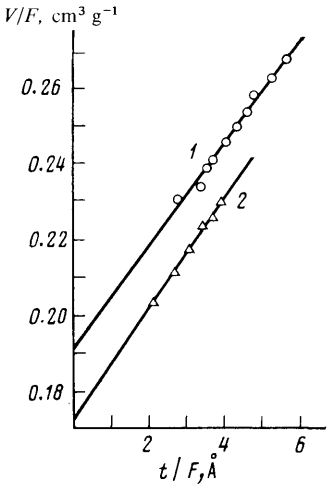


Figure 6. Plots of the t/F method for AU11 active carbon: *1*) nitrogen at 78 K, *2*) benzene at 293 K.[20]

As an example we show in Fig.6 some plots by the t/F method for the AU11 active carbon. According to the almost identical slopes of the two straight lines the specific surfaces of mesopores given by experiments with nitrogen and with benzene are also identical (133 and 140 $m^2\ g^{-1}$ respectively). The micropore volumes of the carbon measured with nitrogen are greater by 0.02 $cm^3\ g^{-1}$ than those measured with benzene. This difference can be explained by the molecular sieve properties of the carbon. Thus the t/F method allows us to determine from a single adsorption isotherm the specific surface of mesopores and the volume of micropores in the adsorbent. The parameter E is obtained from the low relative pressure region ($p/p_S = 10^{-6}-10^{-3}$) of the same isotherm, in which the adsorption on the mesopore surfaces is negligible in comparison to the adsorption in micropores.

In conclusion we should mention the thermodynamic method of determining the specific surface of mesopores from the surface of adsorbed film which disappears when the mesopores are filled by capillary condensation. The method was first formulated by Kistler[21] but its development into a practically useful form is due to Kiselev[22]. The method assumes that the specific surface of the adsorbed multilayer in the mesopores is indistinguishable from the specific surface of the mesopores themselves.

The differential molar heat of adsorption of a vapour initially saturated at the stated temperature is given by Eqn.(6). The ratio of the integral work of adsorption of the vapour between a_0 (the adsorption corresponding to the onset of capillary condensation) and the limiting adsorption a_S for $p/p_S = 1$ to the surface free energy of the adsorbed film σ gives the specific surface area of the adsorbed film S':

$$S' = \frac{1}{\sigma}\int_{a_0}^{a_S} A\,da .$$

The integral is usually evaluated graphically.

Table 5. Specific surface areas ($m^2\ g^{-1}$) of mesopores in active carbons[23].

Active carbon	S_{me}	S'	S_{me}	S'
	benzene, 273 K		nitrogen, 78 K	
AU 10	100	93	95	87
AU 11	140	117	133	105
AU 12	135	157	165	135
AU 13	110	93	90	77
AU 14	197	186	190	166

The specific surface areas of mesopores in highly porous active carbons listed in Table 5 were calculated from experiments with benzene and with nitrogen[23]. The results most closely consistent with experiments for different vapours were obtained by the t/F method. Comparing the average values for each method, the specific surfaces of the adsorbed films are found to be slightly low, as expected from the assumed equality of the surface of the adsorbed film and that of the adsorbent.

In formed zeolites the micropores are part of the zeolite crystallites, and the gaps between crystallites in contact are equivalent to mesopores. Hence the t/F method is applicable (in principle) to formed and to natural zeolites.

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Use of the Classical Trajectory Method in Modelling the Dynamics of Atom-Molecule Collisions in Chemical Reactions

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This review discusses methods of modelling atom - molecule collisions in chemical reactions by calculating the classical trajectories, and the application of these methods in studies of the dynamics and kinetics of bimolecular and unimolecular reactions. The discussion includes methods of defining and analysing the potential energy surface, methods of calculating the trajectories in multidimensional phase space, and statistical methods of controlling numerical experiments (selection of initial parameters, calculation of the distribution function of the active molecule with respect to life-time, etc.). 154 references.

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I. INTRODUCTION. FORMULATION OF THE MOLECULAR DYNAMICS PROBLEM

Rapid progress is being made in experimental and theoretical studies of the kinetics of chemical reactions at the microscopic level. The exchange of energy between different degrees of freedom during molecular collisions and intramolecular motion are being studied as component parts of chemical reactions and of relaxation processes. The formulation of the problem is closely associated with practical aspects of non-equilibrium chemical kinetics: the determination of the rate constants of fast processes and of the role of different degrees of freedom in the kinetics of chemical reactions taking place in strong shock waves and in rarefaction waves, with controlled external stimuli applied to specified degrees of freedom of the reacting molecules, etc. On the other hand, rate constant data for these processes obtained by modern methods of diagnosing initial, intermediate, and final states of reacting gases can be used as the experimental foundations for the solution of the problem.

In addition to quantum-mechanical calculations of the probability of elementary transitions, the theory increasingly uses numerical methods of solving the equations of molecular motion (i.e. the methods of molecular dynamics). In a strict formulation of the problem the motion of an isolated molecule as a whole, and that of its component parts, are described by the Schroedinger equation, which takes into account the interactions of all electrons and nuclei. Molecular dynamics in the widest sense is concerned with the motion of both the nuclear and the electronic subsystem. However, a large class of problems in molecular dynamics and chemical kinetics can be solved by determining only the motion of the nuclei. Under these conditions the electronic subsystem acts as a field of forces in which the nuclear motion takes place, and no allowance for it is needed beyond determining this field.

In the Born–Oppenheimer adiabatic approximation the motions of electrons and of nuclei can be treated separately. The effective interaction between the nuclei is defined by the potential energy surface (PES), which depends on the internuclear distances and on the quantum state of the electronic subsystem. The conditions under which the adiabatic approximation is valid are determined by the difference in energy between the electronic levels and by the velocity of the nuclei, and are characterised by the Massey parameter[1].

The motion of nuclei in a potential field can be studied by classical mechanics. The error associated with the classical approximation can be evaluated by comparing the solutions of the quantum and of the classical motion problem. A detailed analysis of the approach to the classical limit in the theory of molecular collisions is given in Ref.2.

Many workers[3–11] (for example, by using model PES of the LEPS type†) have solved the dynamics problem both within the framework of the classical equations of motion and quantum-mechanically. The two types of solution were used to calculate the probability of elementary transitions with different types of averaging over the initial and the final states. It follows from that work[3–11] that for "reasonable" PES with high activation barriers the difference between the averaged process parameters calculated in the classical approximation or quantum-mechanically is small. Only the classically forbidden processes (for example, tunnelling and reflection above barriers) are exceptional in this respect. These processes involve light atoms, and are very important for the kinetics of reactions at low temperatures. For a wide range of reactions with thermal energies of ~1000 K the classical approximation is adequate.

In Slater's dynamical theory[15] the molecule is treated as a set of classical harmonic oscillators. This model allows analytical treatment, but the harmonic approximation is not even qualitatively correct when used to describe the nature and rate of intramolecular energy redistributions and the localisation of energy along the reaction coordinate. The models used in modern molecular dynamics allow as far as possible for the real interactions in the molecule. Numerical studies of these models by computer calculations provide the modern "experimental" basis for further developments in

†The LEPS potential[12–14] is named after its proposers (London–Eyring–Polanyi–Sato). It is an empirical potential, with many adjustable parameters. In 1929 an attempt was made to construct the potential surfaces for three hydrogen atoms. Subsequently many empirical parameters were introduced into the potential, which gradually lost its quantum-mechanical significance. The LEPS potential is widely used at present to describe three-particle interactions.

dynamical theory. Dynamical calculations for molecules containing more than two nuclei are possible only with the most advanced computing techniques, even within the confines of the classical description (the "classical trajectories method"). The volume of the computational work is so enormous that even on the best computers the problem can be solved only by exploiting new and efficient methods of computing mathematics.

Several review articles on numerical modelling in molecular dynamics using classical trajectory calculations have appeared in the last decade[16–20]. The aim of the present review is to examine the most recent advances in this area and to acquaint the reader with practical results. The second section is devoted to methods of modelling atom–molecule collisions and chemical reactions by using classical trajectories, and the third section deals with the application of these methods to studies of the dynamics and kinetics of bimolecular and unimolecular reactions.

II. METHODS OF STUDYING INTRAMOLECULAR MOTION BY USING CLASSICAL TRAJECTORIES

Three basic tasks can be distinguished in the development of numerical methods of solving the molecular dynamics problem in the framework of the classical equations of motion.

1. Determining the PES. Numerical solution of the Schroedinger equation for complex molecules is impossible at present even on the most modern computers, and therefore the number of non-empirical PES calculations so far reported is very small. Model surfaces which adequately describe the molecular system in the asymptotic regions of phase space are usually employed: the models correctly describe the energetics of the main paths of the reaction, and the vibration frequencies and the geometries of the initial molecule and of the reaction products. By using these PES the general features of the dynamic behaviour of molecular systems can be identified, and methods of numerically modelling the dynamic processes can be developed.

2. Determining the initial conditions. In order to obtain kinetic expressions for analysing the molecular dynamics we must examine a set of trajectories to allow for the statistical nature of the initial data in a real physical experiment. At the same time the number of trajectories must not be too great, since the calculation of each trajectory is very costly in computer time. These conflicting requirements add to the difficulty of determining the initial conditions.

3. The choice of an effective numerical algorithm for solving the classical equations of motion, capable of calculating the trajectory of motion reliably over long integration times. The solutions usually show a large scatter of characteristic times, and are oscillatory functions, but they must keep the integrals of motion constant. As a result, a need for special numerical methods of calculating trajectories has arisen.

The PES can be adequately described in a number of ways. One of these is based on *ab initio* calculations of the potential in a limited region of configurational space.

Leforestier[21] calculated the dynamic characteristics of the reaction $H^- + CH_4 \rightarrow CH_4 + H^-$ by using an *ab initio* potential for a small region of the transition state, and obtained the classical trajectories of motion for a small translational energy along the reaction coordinate. This choice of initial conditions in the region of the transition state leads to rapid dissociation, and the motion is observed only in a limited region of configurational space. Hence this very interesting method does not allow us (unfortunately) to analyse the dynamics of a reaction over the whole of phase space.

From the potential energy at a few reference points, calculated by numerical solution of the Schroedinger equation, and knowing the asymptotic behaviour of the potential, a polynomial surface (called a spline[24]) was calculated[22,23]. This approximation allows wide variations in the PES, while keeping constant the reference points and the general structure, and therefore it offers detailed information on the effect of the shape of the PES on the dynamics and kinetics of the reaction.

As we have already pointed out, the Born–Oppenheimer adiabatic approximation is often used in the classical description of molecular dynamics. However, some molecular processes are strongly non-adiabatic, but this can be allowed for in the dynamical approach. The interactions between two adiabatic energy levels have been studied[25–30], and the classical problem has been solved by first considering only one potential surface but allowing for the probability of transition to another PES (calculated by the Landau–Zener formula[1]) in the region where the two surfaces approach each other closely or intersect. Further classical motion up to the next intersection lines takes place on the old and the new PES with probabilities $1 - P$ and P respectively, and so on. This method of allowing for non-adiabaticity is applicable when the section of the classical trajectory in which transitions between PES have a high probability is relatively short.

The first reported application of the classical trajectory method was to bimolecular collision processes between an atom and a diatomic molecule[31–33], i.e. a special case of the three-body problem. Because of the relatively small number of dimensions of the phase space for a three-body system, fairly detailed computer calculations of the trajectories are possible. The most successful numerical calculations and analyses of classical trajectories so far reported have been in studies of the three-body problem.

The classical trajectory method as applied to collisions between an atom and a diatomic molecule has been described in detail[34] for the exchange reaction $H + H_2 \rightarrow H_2 + H$. The choice of the coordinate system for the classical trajectories is considered in special detail. The initial conditions are chosen so as to describe the quantum states of the reactants as exactly as possible. Equations relating the initial and the final quantum states of the system to the classical variables are given.

Statistical treatment of the calculated trajectories yields kinetic information with a varying amount of detail. The probability of the reaction is first determined, and hence the full cross-section of the reaction as a function of the initial states of the reactants and the final states of the products are obtained. The rate constant of the reaction is then calculated as the integral of the full reaction cross-section for a given distribution of the initial states of the reactants. The thermal (equilibrium) rate constant is calculated by assuming a Maxwell distribution of the molecules with respect to velocity and a Boltzmann distribution with respect to the internal initial states.

Obviously, the results of dynamical calculations can be used in the same way to calculate the rate constants under non-equilibrium conditions, for example for different temperatures of the different degrees of freedom, or for other stated deviations from the Maxwell–Boltzmann distribution. This allows us, in particular, to apply the classical trajectory treatment to non-equilibrium processes in the upper layers of the atmosphere, and also (under laboratory conditions) to the excitation of molecular degrees of freedom by laser radiation or to the excitation of a gas by a laser, by powerful shock waves, or by chemical activation.

Raff and coworkers[35] have developed a method of calculation for the four-centre problem which allows (by a special choice of coordinate system and of initial conditions) the following collisions to be studied: atom–atom, atom–diatomic molecule, atom–triatomic molecule, and diatomic molecule–diatomic molecule. The method has been used to examine various alternative mechanisms of the $I_2 + H_2$ reaction and to calculate the rate constant of the recombination reaction $I + I + H_2 \rightarrow I_2 + H_2$. The calculated constant agrees exactly with experiment.

These methods are valid only for systems in which the number of atoms taking part in the reaction is small. They cannot be applied to reactions involving polyatomic molecules.

A method which can be applied to studies of the dynamics and kinetics of those reactions has been described[36]. Within the limits of the proposed model schemes, different mechanisms for the decomposition of excited molecules can be examined and the conditions for selective and for thermal activation can be defined. For modelling the decomposition of a polyatomic molecule over an activation barrier the following procedure is used to define the initial conditions: the origin of each trajectory is chosen in the region of phase space corresponding to the activated complex, and the trajectories are calculated twice (once for positive and once for negative time changes). By "fusing" these two trajectories the trajectory of the motion of the molecule leading to decomposition is obtained. This method of defining the initial conditions allows a correct choice of the trajectories leading to decomposition, and can be used to calculate the maximum spontaneous decomposition time for each trajectory. The method can also be used to model reactions such as $(AB)^* \rightarrow A + B$ and $A + BC \rightarrow (ABC)^* \rightarrow AB + C$, including those in which the fragments A, B, and C have a complex structure. It has been applied to studies of the decomposition of molecules such as N_2O and CHF_3.[37,38] The practical application of the method requires a knowledge of the geometry of the activated complex. In reactions with a well defined activation barrier the position of the activated complex is usually given by the saddle point of the PES. The directions of the reaction coordinates at the saddle point are the directions of decreasing potential energy.

In dynamic studies of chemical reactions the configuration of the activated complex (reaction path) often needs to be known. If the saddle point of the PES is known, and if the configuration of the activated complex is determined by the saddle point, the identification of the reaction path presents no difficulty. We only need to follow the potential energy surface downwards from the saddle point to the valleys of products and of reactants in the direction of the reaction coordinate. However, the most difficult part of the procedure is to find the saddle point, because paths leading to extrema and to saddle points are not easily identified by using local methods of describing the energy surface.

A localised method of studying the energy surface which nevertheless allows the saddle point to be identified has been described[39]. The step of the algorithm consists in moving along the constant energy surface and searching for the point where the surface is least steep. This method is a mathematical realisation of the idea put forward by Pencir[40]. Another method of searching for the saddle point of the PES[36] relies on a global description of the surface. The PES is intersected by a hyper-plane passing through the valleys of products and of reactants. The descent to the saddle point begins at the point in the section where the potential energy is a maximum. The saddle point in the PES is easily located by this procedure.

If the initial conditions are chosen arbitrarily not all the trajectories lead to reaction: in other words, phase space can be divided into reaction-active and reaction-inactive regions. Dynamical studies[41–43] have established the general condition for distinguishing these two types of region in phase space for reactions of the $A + BC \rightarrow AB + C$ type. This condition depends on the activation energy and on the form of the saddle point in the region of the activated complex.

Statistical methods of evaluating multidimensional integrals are used to calculate rate constants by the classical trajectory methods. The first attempts at calculating the constants relied on the standard Monte Carlo procedure, in which each variable was arbitrarily associated with one particular distribution law, irrespectively of the other variables[34]. More exact methods of calculating the integrals from a limited number of chosen trajectories were subsequently developed. These include a Monte Carlo scheme[44] for modelling the three-particle interaction act. By specifying the initial conditions as suggested it is possible to choose trajectories in the part of phase space which makes the most substantial contribution to the wanted kinetic parameters. The method was used to calculate the rate constant for the $H + H + H \rightarrow H_2 + H$ recombination reaction, which was found to agree with experiment for temperatures between 2000 and 5000 K, as well as giving the distribution in energy of the hydrogen molecules.

A recently developed method of evaluating multidimensional integrals for calculating reaction rate constants[45,46] relies on a non-random sampling of the initial conditions. The error in the calculation of the integral was shown to be smaller than in the standard Monte Carlo method. This allows a smaller number of trajectories to be used to achieve a prescribed level of accuracy in the evaluation of the integrals.

A statistical procedure (the modified method of moments) has been used[47] to calculate the distribution functions with respect to the spontaneous disintegration time of excited molecules. The modification of the standard method of moments consists in limiting the region for which the changes in the arbitrary quantity are calculated. This modification was introduced because the distribution of spontaneous decomposition times for excited molecules gave a set of random values concentrated in a limited range of time, although the true range of spontaneous decomposition times extends over the whole of the positive time axis.

A new procedure[48,49] for choosing initial conditions (importance sampling) offers an even lower error in the calculation of multidimensional integrals. It has been used to calculate the rate constants of the bimolecular reactions $F + H_2$, $C + H_2$, and $O(^3P) + H_2$, and shown to be superior to the standard method.

Some workers[50–52] have avoided the direct calculation of multidimensional integrals by expanding the differential scattering cross-section into a Legendre polynomial series. The coefficients of the expansion are obtained by statistical methods. In this case the evaluation of the multidimensional integral reduces to a statistical calculation of a discrete set of one-dimensional quantities. It has been shown that this method differs from the methods based on the direct calculation of multidimensional integrals in not causing a loss of information when the averaging is carried out over small angles. Some calculations[53–57] of the rate constants of various reactions in terms of flows through the critical surface in phase space have been based on Keck's variational theory[58].

The postulates of the statistical theories can be tested by combining the methods of molecular dynamics with estimates of the kinetic parameters. Dynamical calculations can be

used to confirm the hypothesis of an equilibrium distribution of active molecules in the region of the transition complex, and also to evaluate the transmission coefficients, i.e. to test the interpretation of the rate constant as a flow of representative points through the critical surface in the direction of the reaction products, and finally they can also be used to test the assumed statistical nature of the redistribution of energy in the active polyatomic molecule.

In some recent papers[59-63] the results of the classical trajectory method are compared with those obtained by applying statistical theories to the same PES. Good agreement between the two theories is obtained if the surface has a relatively simple structure, without sharp curvatures or excessively steep slopes.

Other recent papers[64-66] examine the relationship between the redistribution of energy and the stability of the classical motion. An analogue of the Lyapunov function, describing the behaviour of a specially defined gap between trajectories, is used as a criterion of the degree of randomisation of the system. A statistically randomised energy is revealed by an exponential increase in this distance. The degree of ergodicity of the system is determined by the nature of the PES.

A detailed dynamical analysis of the statistical behaviour of molecular systems has been published[67,68]. The degree of ergodicity of a polyatomic molecule is characterised by the spectra of the autocorrelation functions of the generalised momenta of the normal vibrations, obtained in the calculation of the classical trajectories. The area under the spectrum defines the energy of the given normal mode, and energy redistribution processes within the molecule can be characterised by the time-changes in the shape of the spectrum. At low energies the molecule behaves as a set of weakly coupled harmonic oscillators, and the spectra consist of discrete lines, but at higher energies additional lines and a continuum appear in the spectrum.

The autocorrelation function method has been applied in studies of the dynamics of intramolecular energy redistribution in a model of the CD_3X molecule (where X = H, Cl). Different PES were used to model the reaction with and without an activation energy barrier. Initial excitation of the molecule was by chemical or by thermal activation. It was found that the possibility of randomising the initial energy distribution of the active molecule depends on the characteristic features of the PES and on the total energy of the system. An equilibrium distribution of energy among the products is observed if the PES has no barrier in the output channel, and also in cases of strong intermolecular interactions.

Modelling studies of unimolecular reactions of complex molecules are reviewed in Refs.69 and 70. Some universal principles for the construction of model PES are formulated: they allow the equilibrium structure of the molecule, the force constants, and the relative masses of the particles to be varied. Three methods of selecting the initial conditions for polyatomic molecules are discussed: 1) selective excitation of normal modes, 2) non-selective (equal-probability) filling of phase space along the coordinates, 3) gradual selection, each set of initial conditions being used to generate the next set. The last two methods of defining the initial conditions ensure that all additions to the phase space are equally probable (if the number of samples is large enough), and can be used for modelling thermal activation. These principles have been used in a study[70] of the unimolecular decomposition of CD_3Cl, and the results have been compared with those of Ref.68. For small excitation energies it was shown that the polyatomic fragment CD_3 can be treated as a heavy structureless particle.

We should note that in a phase space with a large number of dimensions (~12–15 measurements) the modelling of thermal activation by equal-probability or by gradual selection requires an extremely large number of initial points for filling the phase space with a dense and uniform distribution of trajectories. A dynamical-statistical description of the excited molecules, applicable to barrierless unimolecular decomposition reactions, has been proposed[71] in order to overcome the need to calculate a large number of trajectories to obtain adequate kinetic information. This description is based on assessments of the stability of the distribution of spontaneous decomposition times with respect to variations in the configuration of the critical surface, and it allows the distribution function to be calculated from a relatively small number of trajectories. The distribution over maximum times for spontaneous decomposition can also be obtained from this description of the excited molecules.

To conclude this section we should stress that dynamical descriptions of unimolecular reactions usually deal with long-lived (in comparison to the molecular vibration period) polyatomic systems. This imposes very stringent requirements on the numerical solution procedure applied to the differential equations of motion. The effectiveness of the solution of the classical equations of motion has been improved[45] by an algorithm which allows a system of differential equations to be solved by local linearisation. At each integration step the initial PES is fitted to a parabolic expression. The resulting new system of differential equations is linear, and therefore can be solved exactly. By improving the approximation (i.e. by shortening the integration step) the new solution of the problem can be made convergent over the whole integration range. The additive integrals of motion of the original problem are retained (within the stated precision) in the numerical solution by choosing a parabolic approximation for the PES.

We have described[36] a procedure which allows neighbouring trajectories to be calculated, once the trajectory for the specified initial conditions has been obtained, by expanding the solution of the equation of motion in a Taylor series in increments of the initial data. This procedure allows new trajectories of motion to be obtained at a small additional cost in computer time, and thus it offers a substantially greater volume of data and an effectively filled initial phase space. The effectiveness of these new programs has been compared with that of the previously most widely used procedure: that of Kutta and Meerson. The algorithm proposed in Ref.45 was found to be the most effective for trajectories of motion of polyatomic systems extending over long times and showing a large scatter of characteristic times.

Practical applications of different methods of calculation based on classical trajectories have shown that surfaces which adequately describe experimental results can be constructed by varying the PES parameters and by comparing the results of model calculations with kinetic data.

III. DYNAMIC BEHAVIOUR OF MOLECULES AND KINETIC ASPECTS OF REACTIONS

1. Dynamics of Bimolecular Reactions

The rate constants of chemical reactions and the relaxation times of the associated processes calculated by the classical trajectory method are relatively insensitive to the lack of precision of the classical approach, to the errors of the numerical integration, and to the detailed features of the PES, since they are averaged over many trajectories.

However, both the rate constants and the relaxation times are sensitive to the overall characteristics of the PES.

Polanyi and coworkers[72-82] have carried out an extensive investigation of the effect of the position of the PES barrier on the kinetic behaviour of a molecular system. For exchange reactions such as A + BC → AB + C the PES is classified into different sections along the reaction path. Depending on whether the kinetic energy of the system is converted into internal energy of the products during the approach of the reactants or during the separation of the products, the PES is said to be of the attractive or of the repulsive type. In the intermediate case the surface is called "mixed". PES of the attractive type are shown to be characteristic of exothermic reactions, and those of the repulsive type of endothermic reactions. The energy distribution functions for the products have been determined as a function of the type of surface. Thus, for exothermic reactions the attractive nature of the potential causes strong vibrational excitation of the products. The degree of vibrational excitation of the products is determined also by the mass ratio of the reactants. The effectiveness of rotational and of vibrational excitation in overcoming an activation barrier has also been analysed as a function of the location of the barrier. It was found that the translational energy of the reactants is more effective than their vibrational energy in overcoming barriers located in the reactant region. The vibrational energy of the reactants is converted into vibrational energy of the products with a high efficiency.

Classical trajectory analysis has been used to study a large number of molecular collision processes and to identify their kinetic features. The vibrational transitions in the exchange reactions

$$\begin{aligned} H + H_2(v = 1,2) &\rightarrow H_2(v = 1,2) + H \\ H + HCl(v = 1,2) &\rightarrow HCl(v = 1,2) + H \\ Cl + HCl(v = 1,2) &\rightarrow HCl(v = 1,2) + Cl \end{aligned}$$

have been studied[83] by using the LEPS potential. Vibrational excitation of the initial molecules are shown to lower the activation energy in every case, the magnitude of this effect depending on the combination of nuclear masses. It was also shown that this path to changes in vibrational energy is an efficient vibrational relaxation mechanism in sufficiently dense atomic gases.

The displacement reactions

$$\begin{aligned} Br + HBr &\rightarrow H + Br_2 \\ Cl + HX &\rightarrow HCl + X \\ X &= I, Br \end{aligned}$$

have also been studied[84-88], together with the vibrational relaxation of HCl and DCl in the gas phase. The rate of the reactions was found to be increased by a preliminary vibrational excitation of the reactants. The agreement of these results with those of molecular beam experiments is good on the whole, and confirms the validity of the theory.

Several papers[89-95] deal with vibrational relaxation processes and the role of vibrational energy displacement reactions.

The first attempt at describing the vibrational relaxation of diatomic molecules by classical trajectories related to the O_2 + Ar reaction[96,97]. The potential of the molecule was approximated by the Rydberg–Klein–Rees method. The probabilities of changes in vibrational states and of dissociation of the molecules were calculated over a wide temperature range (from 1000 to 20000 K), in which the probability of one-quantum and two-quantum transitions decreases as the vibrational level number n increases, and for $n \geq 20$ it is independent of temperature. The calculations were satisfactorily consistent with scattering experiments in molecular beams and with direct measurements of relaxation times.

The classical trajectory method has been applied to the relaxation processes in the Br_2 + Ar system[98]. The effect of molecular rotation on the rate of vibrational relaxation was examined, and $V-R$ exchange was shown to be more effective than $V-T$ exchange in this system. Results obtained by the "breathing sphere" and the "rough sphere" model[99] were compared, and recommendations on the relative merits of these models were given.

Another group of papers[100-109] discusses the redistribution of vibrational, rotational, and translational energy in excited diatomic molecules (H_2, N_2, KBr) in their own atmosphere or in an atmosphere of inert gas (Ar, He). The differential transition cross-sections were calculated as a function of the vibrational and rotational quantum numbers, together with the full cross-sections of the transitions from the given quantum states. The effect of variations in the PES on these cross-sections was estimated, and it was shown that the full cross-section is less sensitive to these variations than the differential cross-section. The probability of a vibrational–rotational transition and the characteristic vibrational relaxation time were studied as a function of the initial vibrational energy of these diatomic molecules and of temperature. The limiting value of the total collision energy, for which the rotational relaxation of the diatomic molecule can be expressed in the rigid rotator approximation, was also calculated.

The classical trajectory method has been used in models of interatomic interactions in molecular systems[99,110-112].

Another series of papers[113-116] discusses the reactions

$$\begin{aligned} H + F_2 &\rightarrow HF + F \\ F + H_2 &\rightarrow HF + F \\ HF + H &\rightarrow HF + H \end{aligned}$$

and the corresponding reactions of the deuteriated analogues. The differential reaction cross-sections and the deactivation rate constants were calculated, the distribution of energy among the products was found, and the relative role of translational and rotational energy in the reactions was determined. In the deactivation of HF and DF the vibrational energy was found to be converted mainly into translational energy of the products, i.e. the relaxation occurs by the $V-T$ mechanism, but at higher levels of rotational energy the $V-R-T$ mechanism contributes increasingly to the deactivation.

The effect of the vibrational state of the molecule on the reactive scattering characteristics has been studied[117] for the reactions

$$\begin{aligned} O + N_2 &\rightarrow NO + N \\ O + H_2 &\rightarrow OH + H \\ N + O_2 &\rightarrow NO + O, \end{aligned}$$

and an analytical expression for the rate constant in terms of the initial vibrational energy and of the translational temperature of a diatomic molecule was obtained.

Numerical solutions of the classical equations of motion by the Monte Carlo method have been used[118-126] to calculate the rate constants and the angular and energy distributions of the products for various reactions in triatomic systems:

$$\begin{aligned} H_2 + H &\rightarrow H + H_2 \\ D_2 + F &\rightarrow DF + D \\ O + N_2^* &\rightarrow NO + N \text{ etc.} \end{aligned}$$

Isotope effects and the dependence of the kinetic parameters on the type of PES were also investigated.

The classical trajectory method can be applied to the analysis of reaction mechanisms as a function of the type of PES. From the solution of the dynamical problem the reaction mechanism corresponding to the given PES is determined. The inverse problem can also be solved: to construct a PES consistent with the experimentally established mechanism.

A series of papers[127-131] discusses the study of reaction mechanisms on the basis of dynamical calculations. A special study was made of the recombination reaction Br + Br + E (where E = He, Ar, Xe), assuming:

a) an energy transfer mechanism, i.e.

$$\begin{aligned} &Br + Br \rightleftarrows Br_2^* \\ &Br_2^* + E \rightarrow Br_2 + E\ , \end{aligned}$$

or b) a radical–molecule complex mechanism, i.e.

$$\begin{aligned} &Br + 2E \rightleftarrows BrE + E \\ &BrE + Br \rightarrow Br_2 + E\ . \end{aligned}$$

In a He atmosphere the first mechanism is predominant, and in an Ar or Xe atmosphere the opposite is true. By allowing for both these mechanisms the calculations can be satisfactorily reconciled with experimental data. Dynamical calculations have shown that when the reaction takes place by the energy transfer mechanism the pre-exponential factor of the rate constant is almost independent of temperature, whereas if the radical–molecule mechanism is predominant this factor decreases as the temperature increases.

An example of the determination of the PES parameters from experimental data is given in Ref. 132. The parameters of the PES in the LEPS form for the reaction $O + H_2 \rightarrow OH + H$ were found by minimising the target function $\Phi = \ln(k_r/k_e)$, where k_r is the rate constant of the reaction, calculated by the classical trajectory method, and k_e is the experimental rate constant.

The PES have been constructed[133-135] for four classes of chemical reaction mechanisms of the exchange type $A + BC \rightarrow AB + C$. The influence of special features of the PES on the energy distribution of the reaction products and on the type of reactive scattering was clearly revealed.

We have discussed[37] a model of the decomposition of linear molecules of the N_2O type. The aim was to find the distribution function of the spontaneous decomposition time of the molecules and to investigate the distribution of energy among the reaction products. The distribution function was determined from the maximum spontaneous decomposition times, and it was found (by a numerical experiment) to have two maxima. The first maximum corresponds to the trajectories for elastic scattering, whereas the other trajectories describe the behaviour of the excited molecules. The distribution function of the maximum lifetimes $[f_m(\tau)]$ for these trajectories is satisfactorily described by a gamma-distribution. We found that $f_m(\tau)$ depends on the initial kinetic energy of the vibrational degrees of freedom and on the kinetic energy along the reaction coordinate. According to the assumed model, the initial kinetic energy of the vibrational degrees of freedom (including the reaction coordinate) is converted, on average, into internal energy of the N_2 molecule, whereas the rotational energy appears as kinetic energy of the relative (translational) motion of the products.

A detailed dynamical study of the following reactions has been reported[136,137]:

$$\begin{aligned} &Br + H_2 \rightarrow HBr + H \\ &H + H_2 \rightarrow H_2 + H\ . \end{aligned}$$

The results were compared with those of the statistical theory for the same reactions. The reaction probability P_r was calculated by the classical trajectory method. The probability P_s of the system reaching the transition state was also calculated, and compared with the probability of the reaction obtained by the transition state method (P_{ts}). The transmission coefficient P_r/P_s and the distribution of active molecules in the region of the transition state were found to be strongly dependent on the structure of the PES, and in particular on the location of the barrier. The distribution function of the active molecules in the region of the transition state was determined. For an endothermic reaction with a relatively low barrier located in the valley of the products the probabilities were found to decrease in the sequence $P_{ts} > P_r \cong P_s$. For the reverse reaction ($H + HBr \rightarrow Br + H_2$), on the other hand, we have $P_{ts} \cong P_s < P_r$. For an endothermic reaction with a barrier in the valley of products the transmission coefficient is close to unity, but the distribution function of the active molecules for reactants in their equilibrium state differs from the equilibrium distribution. For exothermic reactions with a barrier in the valley of reactants, e.g.

$$\begin{aligned} &H + H_2 \rightarrow H_2 + H \\ &HBr + H \rightarrow H_2 + Br\ , \end{aligned}$$

the opposite situation exists: the transmission coefficient is smaller than unity, and an equilibrium distribution exists.

2. Dynamics of Unimolecular Reactions

Many recent publications describe studies of unimolecular reactions by numerical methods. A detailed formulation of the problems in the theory of unimolecular reactions which can be solved by the classical trajectory method has been given[138]. One of these problems is the calculation of the distribution function $f(\tau)$ in time (τ) of spontaneous decomposition of molecules. In the RRKM (Rice–Ramsperger–Kassel–Marcus) statistical theory[139] this function is assumed to be exponential for τ values greater than the average vibration period of the thermally activated molecule. To test the validity of this hypothesis and to calculate $f(\tau)$ for a specific molecule as a function of the type of activation and of the parameters of the potential is one of the fundamental problems in molecular dynamics, to which the classical trajectories method is applicable. This problem is very closely related to the validity of the model of weakly coupled harmonic oscillators and of the model of free redistribution of energy between normal vibrations.

The effect of the initial vibrations on the form of the function $f(\tau)$ as a function of the assumed model of the potential has been studied[140] in the case of the dissociation of a triatomic molecule. The calculation was carried out for two models of the potential: harmonic, and anharmonic. Two types of initial state were also considered: 1) a random initial distribution of total internal energy, and 2) the total internal energy is initially finite, and only the kinetic energy is randomly distributed. In the former case the function $f(\tau)$ is found to decrease exponentially with increase of τ for either type of potential, whereas in the latter case this function has a sharp maximum for a harmonic potential and a diffuse maximum for an anharmonic potential.

The influence of anharmonicity on the exchange of energy between modes in unimolecular reactions has been studied[141] in the triatomic CO_2 molecule. The bond energies in this molecule were fitted to a harmonic potential and to a Morse potential. The initial conditions were chosen to give the

molecule a zero total momentum. The interaction between the rotational and the vibrational motion was found to be greater in the case of an anharmonic potential.

The exchange of energy between the normal vibration modes of the triatomic molecules H_2O, O_3, and ClNO has also been studied[142] for different initial excitations of the vibrational and rotational degrees of freedom. According to these calculations there is no exchange of energy between modes when the excitation energy is of the order of one vibrational quantum. As the initial energy of the vibrations increases, the energy of each mode begins to vary, both the amplitude and the rate of this variation increasing with the initial vibration energy.

The spontaneous decomposition of X–C–C–X molecules (where X = H, Cl) has been studied[143–145]. The stretching vibration energy of the bonds for this type of molecule was approximated by a Morse potential, and the bending energy by a potential proportional to the square of the angular variable. The function $f(\tau)$ was calculated for different initial excitations of the molecule. For an equal-probability distribution of the energy over the initial states the distribution function is exponential, i.e. the decomposition is a random process. If only some of the bonds are affected by the initial excitation the function $f(\tau)$ is no longer monotonic, and one of the initially excited bonds is usually the first to break. If the molecule lives long enough, this type of excitation is converted into equal-probability excitation, and the decomposition of the molecule becomes random. From the position of the maximum of the $f(\tau)$ function the duration of the non-statistical behaviour of the system can be calculated. If the maximum occurs at a value of τ significantly shorter than the average lifetime of the molecules the non-statistical behaviour of the system occupies a time much shorter than the decomposition time.

Intramolecular energy redistribution processes have been studied, and the function $f(\tau)$ has been calculated, for the unimolecular decomposition reactions[146,147]

$$C_2H_6 \rightarrow CH_3 + CH_3$$
$$C_2H_6 \rightarrow C_2H_5 + H \ .$$

Calculations by the classical trajectory method and by the statistical theory give divergent results, suggesting that in these reactions the dynamic effects play a predominant role in intramolecular relaxation and unimolecular decomposition processes. Similar conclusions were reached from a study of the methyl isocyanide molecule[148–150].

The dynamical–statistical description has been used[71] to model the unimolecular decomposition of the CH_2FI molecule, which produces[151] strong branching in the fluorination of methyl iodide. The distribution function of the lifetime under chemical activation was obtained for the system: it was found to go through a maximum, and to be satisfactorily approximated by a gamma-distribution. Statistical processing of the experimental results yielded the coefficients of the gamma-distribution, and their dependence on the parameters of the potential. Varying the adjustable parameters of the potential, without affecting the fundamental characteristics of the unexcited molecule, was shown to affect the rate constant of the dissociation by C–I bond breaking. The values of these parameters corresponding to the maximum rate of dissociation were calculated.

The decomposition of the penta-atomic CHF_3 molecule by the biradical mechanism

$$CHF_3 \rightarrow CF_2 + HF$$

has also been modelled[38] for given initial conditions of the activation barrier. Decomposition by a biradical mechanism is typical of a large group of (unimolecular) reactions, and is also important in chain reactions[152]. Modelling a decomposition which yields polyatomic fragments is also of theoretical interest. The main feature of the model used[38] for this reaction is the presence of two negative eigenvalues in the parabolic approximation of the PES at the saddle point, so that the reaction coordinate becomes "two-dimensional". The dynamics of decomposition along a two-dimensional reaction coordinate were studied by numerical methods. Even with this more complex model it was confirmed that when the reaction has a sharply defined activation barrier the position of the activated complex is determined by the saddle point of the PES. Under these conditions the reaction coordinates correspond to eigenvectors of quadratic form which approximate the PES at the saddle point and have negative eigenvalues. The distribution in energy of the reaction products was studied: most of the energy evolved by the decomposition of CHF_3 was shown to be converted into vibrational excitation of the HF molecule. The CF_2 molecule remains practically unexcited.

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The practical realisation (by computer calculations) of the classical trajectory method has provided answers to a number of important problems in the dynamics of polyatomic systems whose solution could not previously be attempted.

Our analysis of recent publications has shown that the study of atom–molecule collisions and of intramolecular motions by the classical trajectory method is potentially applicable to a wide range of chemical reactions.

The number of publications dealing with calculations of classical trajectories is continually rising as a result of the more general availability of powerful computers, of improvements in modelling techniques, and of the easier access to detailed information on the elementary chemical act.

The large fund of data on different classes of reaction, with different potential energy surfaces, allows us to define some general relationships between the fundamental laws of the kinetic process and the characteristic features of the PES. This leads, in turn, to the development of improved models of the PES.

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Thermal Reactions of Polonium

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Published information on the interaction of polonium with the chemical elements has been surveyed and systematised. Attention is paid to specific features of experimental methods for investigating the properties of polonium compounds. Conditions for the direct synthesis of binary polonium compounds and their thermal properties are given. The applicability of the Samsonov classification of chalcogenides to polonium compounds is shown.
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I. INTRODUCTION

The first papers containing communications about phenomena connected with thermal reactions between polonium and chemical elements[1,2] appeared in 1932.

Rona[1] studied the influence of the material of the substrate on which polonium had been deposited electrochemically on the vaporisation of the polonium; vaporisation starts at 280 °C from a gold substrate, at 300 °C from a platinum substrate, and at 550 °C from a palladium one. After a specimen of polonium on a gold substrate had been stored for five months the temperature for the start of the vaporisation of the polonium had increased to 400 °C. Tamman and Löwis of Menar[2] investigated the behaviour of poloniun during the crystallisation of metals by melting filings of silver, copper, lead, bismuth, tin, antimony, cadmium, zinc, or tellurium on which trace amounts of polonium had been deposited electrochemically. Radiographic study of sections of the ingots showed that the polonium is located at the grain boundaries of the metals; it was concluded that polonium differs from other metals in its insignificant tendency to form solid solutions.

The systematic investigation of the thermal reactions between polonium and the chemical elements was begun after milligramme amounts of it had been obtained by irradiating bismuth in atomic reactors.

Detailed information about polonium and its compounds (discovery, distribution, methods of production, physical and chemical properties, state and behaviour in solutions, electrochemistry, analytical chemistry, applications, and safety techniques) has been given in monographs[3-8]. Early American work was surveyed in a review paper[9].

The present review deals with thermal reactions between polonium and the chemical elements which proceed in the interaction of polonium vapour with the liquid or solid elements or the interaction of the gaseous elements with metallic polonium. This information is scattered in the earlier literature. Special attention is paid to works which have appeared in the last decade (after the reviews mentioned above were written). Many experimental investigations have shown that in accordance with its position in the Mendeleev Periodic Table polonium and its compounds exhibit properties close to those of the other chalcogens (especially to tellurium) and their compounds; consequently the material is presented mainly in accordance with the scientific classification of the chalcogenides proposed by Samsonov[10].

II. METHODS OF INVESTIGATION

The use of many contemporary methods of investigation is restricted in working with milligramme amounts of polonium-210 because of the high toxicity of polonium, its ability to form radioactive aerosols, and its tendency to migrate along surfaces; it is also necessary to allow for its high energy release (144 W g^{-1}), the destructive power of the nuclear recoil during radioactive decay (166 TBk g^{-1}) [sic. The energy of the recoiling nucleus is 100 keV (Ed.of Translation)], and the constant accumulation of the radiogenic lead-206 in the specimens (0.5% per 24 h). In addition, the strong α-emission of the polonium brings about ozonisation of the atmospheric oxygen, leading to intense oxidation of the specimens. In working with gramme amounts of polonium the radiogenic heating of the specimens is so great that forced cooling of them is necessary. Safety control of the investigations imposes limitations on the choice of methods (the possibility of carrying out the experiment in glove-boxes, simplicity of the equipment, hermetic sealing of the specimens, and remoteness of the quantitative and qualitative determinations).

Direct vacuum-thermal synthesis[11] in the various versions used industrially was employed in most studies of the interaction of polonium vapour with the chemical elements. In some papers[12] it is called the differential-thermal or ampoule method.

X-Ray powder diffraction, metallographic (determination of the microhardness of layers and their dimensions), and tensimetric (various versions) methods were used for studying some of the properties of the polonium compounds obtained. The composition of the vapour during the heating of the specimens was usually determined by the simplest method—from the sublimation temperature of the condensed vapour. In some investigations the atomic ratio of a component of the vapour was found by using radioactive nucleides and determining their amounts with a γ-spectrometer or the mass characteristics of the vapour found with a mass spectrometer. The melting points of the lanthanide polonides were determined with an optical pyrometer from the change in the emissivity of tungsten when the powder of the compound being studied was deposited on it. The amount of polonium in the specimens was determined calorimetrically or radiometrically.

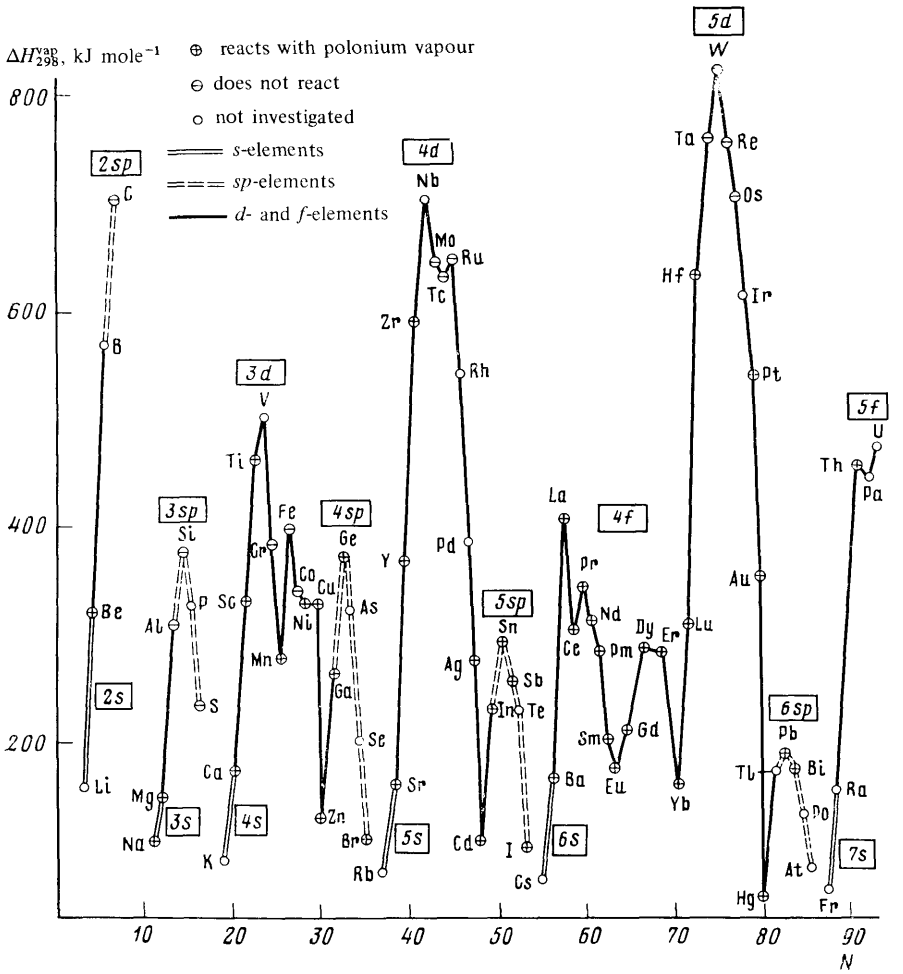


Figure 1. Periodic change in the heats of vaporisation of the chemical elements as a function of their atomic number.

III. CHEMICAL AND PHYSICAL PROPERTIES OF POLONIUM

According to its position in Group VI of the Periodic Table and its electronic structure ...$5s^25p^65d^{10}6s^26p^4$, polonium has a valence shell of six electrons; consequently it (like all the chalcogens—the representatives of this group) can have the following valence states: −2, +2, +4, +6. In accordance with the general rule, the stability of the +6 state becomes weaker with increase in the atomic number of the element along the series of chalcogens. Polonium(IV) is formed under extreme conditions (high concentrations or pressures of the oxidants) and is unstable under ordinary conditions. The existence of polonium exhibiting a valency of −2 (hydride, dimethylpolonium, alkali and alkaline earth metal polonides), +2 (halides), or +4 (dioxide, halides) has been proved in many investigations. The +4 valence state is most characteristic of polonium.

The appearance of the great "metallicity" of polonium in comparison with the other, lighter chalcogens is connected with the decrease in the energetic stability of the s^2p^4-configuration of the outer electrons as the number of the element is increased. This is shown by the periodicity of the change in the enthalpy of vaporisation of the elements (as a measure of the energetic stability of the solid substance in relation to its passage into the gaseous state) as a function of the atomic number of the element (Fig.1). As Fig.1 shows, the enthalpy of vaporisation of polonium is considerably less than those of sulphur, selenium, and tellurium, which corresponds to the general rule for *s*- and *sp*-elements. However, for the *d*- and *f*-elements an increase in the enthalpy of vaporisation with the atomic number is observed. The similarity of the energetic stabilities of the outer electron shells of the 6*sp*-elements is responsible for the similarity in their physical properties.

The temperature dependence of the vapour pressure of polonium was determined by direct (with a Bourdon manometer)[13] and indirect-static (from the radiometrically determinable amount of vapour in a known volume, assuming that polonium vapour is monatomic)[14] methods and is expressed by the equation

$$\lg p[\text{Pa}] = A - B/T, \qquad (1)$$

with the following coefficients:

t, °C	A	B
438—745	9.3545±0.0068	5377±6.7
368—604	9.46±0.05	5440±60

The heats of vaporisation of polonium calculated from equations with these coefficients are 103 and 104 kJ mole^{-1} respectively. The slight difference between the vapour pressures calculated from the results of these methods shows there is a small proportion of diatomic molecules in polonium vapour. The existence of Po_2 molecules has been established spectroscopically[15].

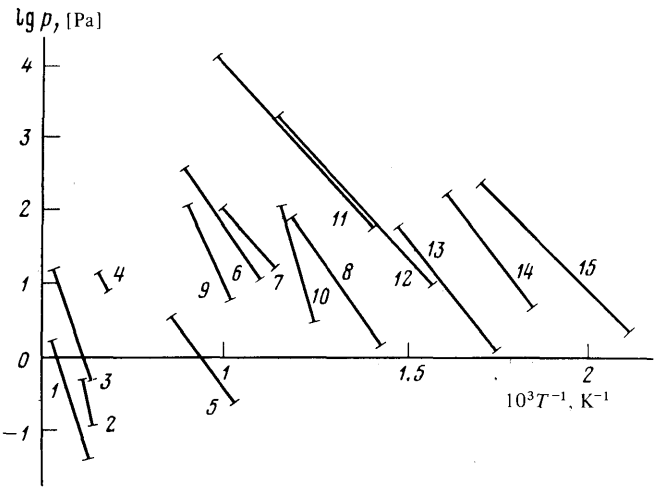


Figure 2. Vapour pressure of polonium above the polonides: *1*) yttrium; *2*) holmium; *3*) dysprosium; *4*) scandium; *5*) hafnium; *6*) lead; *7*) gallium; *8*) indium. Vapour pressure of polonium dioxide during vaporisation (*9*) and its dissociation (*10*); vapour pressure of polonium according to Brooks[13] (*11*) and Abakumov and Ershova[14] (*12*); vapour pressure of polonium hexa-, tetra-, and di-iodides (*13*, *14*, and *15*).

IV. INTERACTION OF POLONIUM WITH THE CHEMICAL ELEMENTS

From a consideration of the peculiarities of the electronic structure, bond type, and properties Samsonov[10] proposed a principle for the classification of the chalcogenides, in which they are divided into three main groups: (1) chalcogenides of metals having outer *s*-electrons in a completed shell, or more deeply lying incomplete electron shells with an ionic–covalent type of bond; (2) chalcogen compounds of elements having outer *sp*-electrons with a covalent–ionic type of bond; (3) chalcogenides of the transition metals having completed *d*- and *f*-electron shells, with a covalent-metallic type of bond in the superposition of a definite fraction of ionic bond.

For convenience in finding general rules the information on the interaction of polonium with the chemical elements and the properties of its compounds are grouped in the present review in accordance with Samsonov's classification. Special attention is paid to polonium compounds with hydrogen and helium.

Hydrogen does not react with polonium when heated. A volatile polonium hydride is formed in insignificant amounts by the action of 0.2 *N* HCl on magnesium foil on which polonium had been deposited and is released from solution when nitrogen, hydrogen, or oxygen is bubbled through. Polonium hydride is formed in lower yield (0.2%) when magnesium powder is added to an acid solution containing trace amounts of polonium. An even lower yield of hydride is obtained by the action of acid on zinc on which trace amounts of polonium had been deposited. Polonium hydride is condensed at −84 °C, its melting point is −36 °C, and boiling point +35.5 °C; it is an unstable compound and belong to the group of covalent hydrides with weak molecular bonds.

Helium forms a volatile compound with polonium under the action of an electric discharge at reduced pressure (0.4–1 kPa). A high temperature favours the occurrence of this reaction[3]. The existence of such a compound is questionable. Probably, we are speaking about the reaction of polonium with He^+ ions, isoelectronic to hydrogen, which can arise in the electric discharge.

1. Polonides of the *s*-Metals

The thermodynamic characteristics of the polonides of the alkali and alkaline earth metals, calculated by Krestov[16], are given below:

Polonide	Na_2Po	K_2Po	Rb_2Po	Cs_2Po	MgPo	CaPo	SrPo	BaPo	RaPo
$-\Delta H^\circ$, kJ mole^{-1}	347	368	335	343	54	255	268	305	284
$-\Delta G^\circ$, kJ mole^{-1}	343	364	335	339	54	255	268	305	284
S°, J mole^{-1}K^{-1}	138	163	186	202	83	95	110	119	127

Sodium polonide Na_2Po (f.c.c. lattice of CaF_2 type, a = 7.473 Å, density 4.08 g cm^{-3}) is observed in specimens of polonium which have been stored in Pyrex capillaries[15]. When an alkaline solution of sodium dithionite containing polonium acts on elemental tellurium at 80 °C and is then crystallised at 0 °C, 40% of the polonium passes into the sodium telluride crystals from the solution. The distribution of polonium in the crystal is constant, which shows isomorphous cocrystallisation and confirms the formation of sodium polonide[17].

Beryllium polonide BePo (a black substance, f.c.c. lattice of ZnS type, a = 5.838 Å, density 7.3 g cm^{-3}) is formed when beryllium is heated (600 °C) in polonium vapour. It is volatile at temperatures above 600 °C.[12]

Magnesium polonide MgPo (a black substance, hexagonal lattice of NiAs type, a = 4.345 Å, c = 7.077 Å, density 6.7 g cm^{-3} [12]) is formed when magnesium is heated (350–450 °C) in polonium vapour. It is volatile at 650 °C and is condensed as magnesium polonide[1].

Calcium polonide CaPo (a grey nonmetallic substance, f.c.c. lattice of NaCl type, a = 6.514 Å, density 6.04 g cm^{-3}) is formed when calcium is heated (550 °C) in polonium vapour. It is volatile at temperatures above 600 °C.[12]

Strontium polonide SrPo (grey metallic substance, f.c.c. lattice of NaCl type, a = 6.796 Å, density 6.3 g cm^{-3}) is formed when strontium is heated (500 °C) in polonium vapour. It is volatile at temperatures above 650 °C.[12]

Barium polonide BaPo (grey metallic substance, f.c.c. lattice of NaCl type, a = 7.119 Å, density 6.3 g cm^{-3}) is formed when barium is heated (525 °C) in polonium vapour. It is volatile at temperatures above 650 °C.[12]

Copper polonide is formed by the condensation of polonium vapour on copper. At 400 °C it is unstable and volatilises[12].

Silver polonide Ag_2PO? (orthorhombic, a = 1.327, b = 5.565, c = 1.404 Å) was obtained in 1950 when silver was heated (400 °C) in polonium vapour. It decomposes at

559 °C.[9] Reliable X-ray diffraction results have not been obtained[12].

Gold dissolves polonium vapour at a temperature above 650 °C; the solubility depends on the temperature of the gold and the vapour pressure of the polonium[12].

Zinc polonide ZnPo (f.c.c. lattice of ZnS type, $a = 6.309$ Å, density 7.2 g cm^{-3}) is formed when zinc is heated (550 °C) in polonium vapour. It sublimes at 400 °C. The saturated vapour pressure of zinc polonide at 500 °C is ~13 Pa.[12] It was first obtained in 1947.[15]

Cadmium polonide CdPo (f.c.c. lattice of ZnS type, $a = 6.665$ Å, density 7.2 g cm^{-3}) is formed when cadmium is heated (550 °C) in polonium vapour. It sublimes at 525 °C. The saturated vapour pressure of cadmium polonide at 500 °C is ~13 Pa.[12]

Mercury polonide HgPo (black crystalline substance, f.c.c. lattice of NaCl type, $a = 6.25$ Å, density 11.1 g cm^{-3}) is formed when polonium is heated (200–325 °C) in mercury vapour. It sublimes at 400 °C. The saturated vapour pressure of mercury polonide at 300 °C is ~13 Pa. An amalgam of mercury polonide is formed in the presence of an excess of mercury[12].

2. Compounds of Polonium with the *sp*-Elements

Aluminium in the solid state does not react with polonium vapour[18].

Gallium polonide GaPo (orange metallic substance) is formed when liquid gallium is heated (340–470 °C) in polonium vapour. Under these conditions a stationary concentration of polonium in gallium is reached, 51–52 at.% (the system can be regarded as a solution of polonium in gallium monopolonide, from which volatilisation of polonium starts at 420 °C). The temperature dependence of the dissociation pressure of gallium monopolonide at 605–735 °C and polonium concentrations of 50–39 at.% is described by Eqn.(1) with the coefficients: $A = 7.39 \pm 0.72$ and $B = 5410 \pm 670$. The enthalpy of the process is 103 ± 13 kJ mole^{-1}. At polonium concentrations <39 at.% the vaporisation of polonium depends on its concentration in the melt, which shows the formation of a solution[19].

Indium polonide InPo (bluish metallic substance) is formed when liquid indium is heated (340–490 °C) in polonium vapour. Under these conditions a constant concentration of polonium in indium (50 at.%) is achieved and is retained, but a loss of indium (and polonium correspondingly) from the specimen is noted. After equilibrium had been reached in the ampoule between the polonium condensate and the specimen it was found that the polonium condensate contained ~40 at.% of indium, which corresponds to the composition of indium sesquipolonide In_2Po_3; the latter seems to be volatile at 490 °C. The temperature dependence of the dissociation pressure of indium monopolonide at 425–575 °C and polonium concentrations of 47–41 at.% is described by Eqn.(1): $A = 9.87 \pm 0.16$, $B = 6740 \pm 120$. The enthalpy of the process is 129 ± 3 kJ mole^{-1}. At polonium concentrations <41 at.% the vapour pressure depends on its concentration in the melt, showing the formation of a solution[19].

Carbon does not react with polonium vapour during heating to 700 °C.[12]

Silicon does not react with polonium vapour during heating to 850 °C.[20]

Germanium starts to absorb polonium vapour when it reaches the melting point (940 °C). The amount of polonium absorbed by the germanium depends on the pressure of the polonium vapour. Raising the temperature of the melt to 980 °C leads to release of the polonium. It is assumed that polonium dissolves in the molten germanium[11].

Tin polonide is formed during the heating of molten tin (370–455 °C) in polonium vapour. After a layer of tin polonide (30 μg mm^{-2}) has formed on the surface the reaction rate is reduced by a factor of ~100, despite the temperature being raised to 590 °C, showing the low solubility of tin polonide in tin. Release of polonium from the resulting specimen on heating starts at 670 °C.[20]

Lead polonide PbPo (f.c.c. lattice of NaCl type, $a = 6.59$ Å, density 9.6 g cm^{-3}) is formed when lead is heated (350 °C) in polonium vapour and also appears in the condensate of metallic polonium during its α-decay[12]. The temperature dependence of the vapour pressure of lead polonide at 640–850 °C is described by Eqn.(1) with $A = 9.06 \pm 0.07$, $B = 7270 \pm 80$. The enthalpy of vaporisation is 139 ± 2 kJ mole^{-1}. When more than 3% radiogenic lead has accumulated in polonium the vapour pressure of the latter falls, negative departures from the vapour pressures calculated by Raoult's law being observed[14].

Nitrogen does not react with polonium during heating to 850 °C, since the polonium sublimes in an atmosphere of nitrogen without undergoing any changes[21]. An explosive polonium nitride is probably formed when ammonium hexabromopolonate(IV) is heated (200 °C).[22].

Antimony in the solid state starts to absorb polonium vapour at 340 °C; the process takes place more vigorously at 470–600 °C. When heated in a vacuum, antimony containing 7.5 at.% polonium starts to lose polonium at 420 °C. During vacuum distillation (600 °C) separation of the polonium and antimony is observed as distinct condensation rings, which shows that an alloy is formed[11].

Bismuth starts to absorb polonium vapour at 350 °C; the Bi–Po phase is assigned two structures: rhombohedral ($a = 4.456$–4.503, $c = 3.602$ Å) and f.c.c. ($a = 3.602$ Å), but there are no definite results for this system[18]. Analysis, by pyrochemical and distillation methods, of the polonium isolated from irradiated bismuth shows that a high degree of separation could be achieved but the polonium could not be completely freed from bismuth[7].

Polonium dioxide is formed slowly from the elements without additional heating, but this reaction is most vigorous at 250 °C. The composition of the oxide was determined from the change in oyxgen pressure during the oxidation of polonium[23]. When polonium dioxide is heated its colour changes gradually from pale yellow to reddish brown owing to a change in the structural modifications (yellow: f.c.c. lattice of UO_2 type, $a = 5.626$–5.687 Å; red: tetragonal, $a = 5.44$, $c = 8.34$ Å [23,24]). Polonium dioxide dissociates in a vacuum at 500 °C. The temperature dependence of the saturated vapour pressure of polonium during the dissociation of polonium dioxide (530–595 °C) is described by Eqn.(1) with $A = 21.57 \pm 0.71$, $B = 16\,920 \pm 500$. The enthalpy of the process is 324 ± 10 kJ mole^{-1}.[25]

Polonium dioxide starts to vaporise in oxygen at 690 °C. The temperature dependence of its saturated vapour pressure in oxygen (700–835 °C) is described by Eqn.(1) with $A = 11.13 \pm 0.11$, $B = 10\,070 \pm 150$. The enthalpy of vaporisation is 192 ± 3 kJ mole^{-1}. An oxygen pressure of 8.7 Pa is required to suppress the thermal dissociation of polonium dioxide at 500 °C, but 13 kPa is needed at 790 °C.[26] The coefficients of the temperature dependence of the polonium dioxide vapour pressure in the interval 718–932 °C were determined by a transpiration method: $A = 14.69 \pm 0.46$, $B = 14\,270 \pm 510$. The enthalpy of the process at 825 °C is 273 ± 10 kJ mole^{-1}.[27]

However, perhaps Steinmeyer and Kershner[27] were not observing the dissociation of polonium dioxide, as is shown by the similarity between the enthalpy of vaporisation they obtained[27] and the enthalpy of vaporisation of polonium dioxide with simultaneous flow dissociation (264 kJ mole^{-1}).[26]

Sulphur does not react with polonium. Polonium sulphide PoS is precipitated by hydrogen sulphide from acidic solutions of polonium and decomposes when heated (275 °C) in a vacuum[3].

Fluorine. Volatile polonium hexafluoride could not be obtained by the fluorination of polonium[9]. Metallic polonium is readily soluble in hydrofluoric acid, probably with the formation of fluoro-complexes. A white solid substance (probably polonium tetrafluoride) is formed by the action of dilute hydrofluorice acid on polonium hydroxide or tetrachloride[3,15].

Polonium dichloride and tetrachloride are obtained as a mixture by direct synthesis from the elements at 125–200 °C. At low chlorine pressures and temperatures polonium dichloride is formed preferentially (ruby-red substance, orthorhombic); at high chlorine pressures and temperatures polonium tetrachloride (lemon-yellow substance, monoclinic or triclinic) is formed. Polonium dichloride is more volatile than the tetrachloride therefore they can be separated by sublimation[9]. Polonium tetrachloride in a medium of chlorine melts at 300 °C with the formation of a pale yellow melt; the melt becomes ruby-red at 350 °C, possibly as a result of decomposition to the dichloride, and at 390 °C it boils with the release of purple-brown vapours, which become bluish green above 500 °C, probably owing to a change in the degree of association. In a vacuum, polonium tetrachloride decomposes at 200 °C to the dichloride, which sublimes in an atmosphere of nitrogen at 190 °C with slight decomposition. Polonium dichloride is reduced to the metal during prolonged heating in hydrogen or hydrogen sulphide[28].

Polonium tetrabromide (bright red) is obtained when metallic polonium is heated (250 °C) in bromine vapour (27 kPa) and melts in a medium of bromine at 330 °C with the formation of a dark liquid, which broils at 360 °C. Polonium tetrabromide decomposes to the dibromide in a vacuum at 200 °C and is reduced to the dibromide by hydrogen sulphide (without heating) and sulphur dioxide (on heating). Polonium dibromide (purple-brown) sublimes in a vacuum at 110 °C and melts at 270–280 °C in a sealed volume (nitrogen atmosphere), probably with disproportionation[22].

Polonium tetraiodide (black) is formed when metallic polonium is heated (40 °C) in iodine vapour (133 Pa) and sublimes in an atmosphere of nitrogen at 200 °C with partial decomposition to the metal. Polonium tetraiodide is reduced to the metal when heated in hydrogen sulphide and does not react with ammonia[29]. When heated, polonium tetraiodide dissociates into polonium di-iodide and iodine. The temperature dependence of the vapour pressure of polonium di-iodide at 200–315 °C is described by Eqn.(1): $A = 10.7 \pm 0.71$, $B = 4905 \pm 362$. The enthalpy of the process is 93.7 kJ mole^{-1}.

At an iodine pressure of 4–9 kPa polonium hexaiodide is formed in the condensed phase; it dissociates into polonium tetraiodide and iodine when heated. The temperature dependence of the vapour pressure of polonium tetraiodide at 270–350 °C is described by Eqn.(1) with $A = 12.75 \pm 0.52$, $B = 6533 \pm 300$. The enthalpy of the process is 125 kJ mole^{-1}. At an iodine pressure of 101–147 kPa the temperature dependence of the vapour pressure (probably of polonium hexaiodide) at 300–540 °C is described by Eqn.(1) with $A = 10.94 \pm 0.48$, $B = 6200 \pm 300$. The enthalpy of the process is 119 kJ mole^{-1}.[30]

3. Polonides of the *d*- and *f*-Metals

Lanthanide polonides are obtained by heating these metals in polonium vapour. Table 1 shows that the sesquipolonides Ln_2Po_3 are obtained after 1–10.5 h at 1000 °C; the monopolonides LnPo are formed after 0.75–2 h at lower temperatures.

Table 1. Synthesis temperatures (t) and melting points (M.p.) of the lanthanide polonides (n = atomic radio Po/Ln).

Ln	t, °C	n	M.p., °C	n	M.p., °C
	According to Refs.31 and 32			According to Ref.33, t = 1000 °C	
Sc	—	—	—	1.59	⩾1840
Y	1000	1.03	1700	1.67	⩾1700
La	600	1.0	1457	1.60	1620
Ce	600	1.08	1430	1.57	1540
Pr	600	1.16	1235	1.56 *	1442
Nd	600	1.05	1423	1.62	1460
Pm	850	1.0	1292	—	—
Sm	600	0.87	1474	1.55	1495
Eu	800	0.81	1488	1.55	1670
Gd	600	1.07	1675	1.55	1635
Tb	700	0.82	2000	1.59	⩾1370
Dy	800	1.02	2048	1.57	2330
Ho	700	0.80	1760	1.58	⩾1460
Er	700	0.73	2081	1.59	⩾1435
Tm	800	1.09	2200	1.59	>2040
Yb	800	0.82	2212	1.57	>2400
Lu	1000	1.02	1898	1.56	1898

*t = 900 (Ref.33).

After reaction with polonium the lanthanide powders have become black and finely dispersed[31] and their specific volume is either retained (lanthanum, gadolinium) or doubled (praseodymium, samarium, dysprosium, holmium). The compounds of polonium with cerium or erbium give a dark red luminescence; those with gadolinium or lanthanum give red; with yttrium, orange; with erbium or scandium, yellow; with thulium, pale yellow; and with lutetium, light green; the compounds with terbium, neodymium, and yttrium do not emit light[33]. All the lanthanide polonides melt incongruently with a great loss of polonium. The promethium[32], samarium, terbium, dysprosium, holmium, thulium, ytterbium, lutetium[31], and yttrium[34] monopolonides have NaCl-type f.c.c. lattices, scandium monopolonide an NiAs-type hexagonal lattice[35].

The start of the reaction between polonium vapour and certain lanthanides is observed at lower temperatures (praseodymium 400 °C, gadolinium 500 °C,[11] scandium 850 °C,[36] yttrium 350 °C [37]). The mean reaction rate of polonium

vapour with yttrium at 700 °C is 6.2×10^{-3}, that at 900 °C is 0.13 μg mm^{-2} h^{-1},[38] but the rate is higher (0.34 μg mm^{-2} h^{-1}) during the most vigorous part of the process[39]. The interacetion of the polonium takes place frontally both at the yttrium grain boundaries and within the grains. After metallographic examination a quantitative estimate of the layers of yttrium polonide for yttrium shows the formation of the monopolonide—a black, crumbling and fragmenting substance with a lower microhardness (84–93 kgf mm^{-2}) than yttrium (103–137 kgf mm^{-2}).[38] The temperature dependence of the polonium vapour pressure during the dissociation of yttrium monopolonide (1300–1600 °C) is described by Eqn.(1) with $A = 8.52 \pm 0.13$ and $B = 15\,600 \pm 190$. The heat of dissociation is 298 kJ $mole^{-1}$. The radiogenic lead which accumulates and the care in setting up the experiment [sic] have no significant influence on the results in the determination of the dissociation pressure of yttrium polonide[37]. The temperature dependences of the vapour pressure above scandium, dysprosium, and holmium polonides are described by Eqn.(1) with the coefficients:

Polonide	Sc	Dy	Ho
t, °C	1200—1250	1300—1600	1300—1350
A	6.83	8.90	17.88
B	8695	14509	29543
ΔH kJ $mole^{-1}$	166	277	565

During the vaporisation of polonium from these polonides, the lanthanide is vaporised simultaneously[36]. The great differences in the enthalpies of the processes (ΔH) show that they are different (vaporisation, dissociation, and probably association, respectively).

Mass-spectrometric investigations of the thermal stability and of the vaporisation of lanthanum, neodymium, gadolinium, and dysprosium monopolonides showed that their vaporisation is incongruent, with decomposition into the elements. Appearance of polonium vapour starts to be observed at 1300 °C for lanthanum polonide, at 1100 °C for gadolinium polonide, at 1040 °C for dysprosium polonide, and 850 °C for neodymium polonide[40].

Thorium polonide is formed when thorium is heated (700 °C) in polonium vapour, the mean reaction rate at 700 °C being 3.1×10^{-3} mg mm^{-2} h^{-1}. The interaction takes place at centres[38].

Titanium monopolonide (NiAs-type hexagonal lattice) is formed when titanium is heated (540–550 °C) in polonium vapour; it dissociates at ~700 °C.[41] The loss of polonium from titanium polonide starts at 650 °C; it is almost complete after 8 h at 710 °C.[42]

Zirconium monopolonide (NiAs-type hexagonal lattice) is formed when zirconium is heated (460 °C) in polonium vapour; it dissociates at ~700 °C.[41]

Hafnium monopolonide (NiAs-type hexagonal lattice) is formed when hafnium is heated (380–400 °C) in polonium vapour; it dissociates at ~700 °C.[41] The temperature dependence of the polonium vapour pressure in the dissociation of hafnium polonide (700–900 °C) is described by Eqn.(1) with $A = 5.91 \pm 0.05$ and $B = 6335 \pm 704$. The enthalpy of the process is 121 kJ $mole^{-1}$.[43]

Table 2. Interaction of polonium vapour with the chemical elements.

Li	Be+ 600 >600 1						H— ind	He+					B	C— to 700	N— to 850 ind	O+ 250 500 *d* 0.5	F ind	Ne
Na+ 0.5	Mg+ 350 650 *v* 1												Al— to 700	Si— to 850	P	S— Ind	Cl+ >125 190 0.5; 0.25	Ar
K	Ca+ 550 >600 1	Sc+ 850 1040 *v* 1	Ti+ 540 700 *d* 0.9	V	Cr— to 1000	Mn+ 350 660 *d*	Fe— to 700	Co— to 900	Ni+ 350 >500 *v* 1—2	Cu+ — 400 *d* —	Zn+ 550 400 *v* 1	Ga+ 340 420 *d* 1	Ge+ 940 980 *d* —	As	Se	Br+ 250 200 *d* 0.25	Kr
Rb	Sr+ 500 >650 1	Y+ 350 1300 *d* 1	Zr+ 460 700 *d* 0.95	Nb	Mo— to 1600	Tc— to 1000	Ru— to 1050	Rh	Pd	Ag+ 400 559 *d* 0.5	Cd+ 550 525 *v* 1	In+ 340 420 *d* 1	Sn+ 370 670 *d* —	Sb+ 340 420 *d* —	Te	I+ 40 200 *d* 0.25	Xe
Cs	Ba+ 525 >650 1	La+ 600 1300 *d* 1	Hf+ 380 700 *d* 0.92	Ta— to 1600	W— to 1600	Re— to 1040	Os— to 1050	Ir	Pt+ — >450 *d* 2	Au+ >650 — —	Hg+ 200 400 *v* 1	Tl	Pb+ 350 700 1	Bi+ 350 — —	Po	At	Rn
Fr	Ra	Ac	Ce+ 600 — 1	Pr+ 400 >1050 1	Nd+ 600 850 *d* 1	Pm+ 850 — 1	Sm+ 600 — 1	Eu+ 800 — 1	Gd+ 500 1100 *d* 1	Tb+ 700 — 1	Dy+ 800 1040 *v* 1	Ho+ 700 1300 *v* 1	Er+ 700 — 1	Tm+ 800 — 1	Yb+ 800 — 1	Lu+ 1000 — 1	
Lanthanides																	
Actinides			Th+ 700 — —	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Notes: "+" = reacts with polonium vapour; "–" = does not react; investigated up to t, °C; "ind." = synthesised by an indirect route. In the first row is shown the temperature for the start of synthesis; in the second row, the vaporisation (v) or dissociation (d) temperature; in the third row, the atomic ratio of polonium to the element.

Manganese polonide is formed when manganese is heated (350 °C) in polonium vapour; it dissociates at 660 °C.[11] It was found earlier[9] that a large number of phases is probably formed in the manganese–polonium system, but a single hexagonal lattice is observed.

Nickel polonide is formed when nickel is heated (300 to 600 °C) in polonium vapour. The polonium : nickel atomic ratio in the compound varies between 1 and 2 and the lattice (NiAs-type hexagonal) parameters are variable. Nickel polonide is extremely volatile, it condenses at 500 °C, and its melting point is ~625 °C.[12]

Platinum polonide $PtPo_2$, obtained in 1949, probably has a hexagonal lattice of $Cd(OH)_2$ type and decomposes at 450 to 600 °C.[9]

Tantalum, molybdenum, tungsten (up to 700 °C), *chromium* (up to 1000 °C),[39] *rhenium* (up to 1040 °C),[11] *cobalt* (up to 900 °C), *technetium* (up to 1000 °C), *ruthenium, osmium* (up to 1050 C),[19] and *iron*[3] do not react with polonium vapour when heated to the temperatures stated in parentheses.

Tantalum, molybdenum[36,37] and tungsten[31,33] are used as materials of construction for supporting polonium preparations in high-temperature investigations, therefore it can be considered that these metals do not react with polonium, at least up to 1600 °C.

V. CONCLUSION

The interaction of polonium with most of the chemical elements has now been studied (cf. Table 2). All the alkali and alkaline earth metals investigated, which comprise the *s*-group elements, and the elements of the copper and zinc subgroup react with polonium to form the corresponding polonides.

The *sp*-elements investigated, when in liquid or gaseous state, react with polonium. The exceptions are nitrogen and sulphur probably because of the strong molecular bonds in these elements. The *sp*-metals and semimetals form unstable compounds which decompose rapidly. Beyond the limits of existence of these compounds, solutions are formed. Gaseous oxygen and the gaseous halogens react with metallic polonium to form the corresponding dioxide or halides of various compositions.

The *d*- and *f*-transition metals behave variously in their interaction with polonium vapour. The lanthanides form the most stable compounds. The metals of the IVB subgroup also form compounds, but their thermal stability is lower. The other metals investigated do not react with polonium. Because of the peculiar electronic structures of manganese, nickel, and platinum they are exceptions and do form compounds with polonium.

In most of the investigations the properties of the polonium compounds are compared with the properties of the tellurium compounds and their similarity is reported in accordance with the position of polonium in the Periodic Table.

Despite the considerable number of papers on the thermal reactions of polonium which have now been published there have been relatively few studies of its binary compounds and these are limited by the specific features of this element and the experimental difficulties in carrying out such investigations.

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Advances in Enantioselective Hydrogenation in the Presence of Chiral Complexes of Rhodium, Palladium, and Cobalt

E.I.Klabunovskii

Data on the enantioselective hydrogenation of the C=C and C=O bonds in prochiral compounds in the presence of homogeneous and heterogeneous chiral complexes of rhodium, palladium, and cobalt are surveyed. They are examined from the standpoint of the influence of the structure of the ligand on the asymmetric effectiveness of the complex.
The bibliography includes 90 references.

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I. INTRODUCTION

A new field of homogeneous catalysis—enantioselective reactions under the influence of chiral metal complex catalysts—has arisen recently and has been developing successfully. Such processes became possible after Wilkinson's rhodium—phosphine catalysts were converted in 1968 into chiral catalysts[1-4] by introducing into them chiral phosphines, the method of synthesis of which had just been developed. In the first studies[5,6] it was already shown that catalysts based on rhodium—phosphine chiral complexes exhibit an appreciable enantioselectivity not only in hydrogenation but also in many other reactions. Subsequently catalytic systems were found which effect asymmetric syntheses on the basis of certain prochiral substrates with an optimum yield reaching up to 95-99%.[4,7] These studies dealt mainly with the hydrogenation of the C = C bond in prochiral compounds, leading to optically active aromatic hydrocarbons or acids. The enantioselective hydrogenation of the C = O and C = N bonds in the presence of rhodium complexes as well as the use of chiral complexes of cobalt, nickel, and palladium as hydrogenation catalysts have been less thoroughly studied.

The enantioselective hydrogenation of acylaminoacrylic acids is of special interest as a method of synthesis of optically active natural aminoacids. In the study of this reaction, which is of practical importance and at the same time serves as a model, attention was concentrated on the selection of an effective ligand for rhodium complexes.

In the synthesis of new chiral ligands the availability of the initial optically active compounds is a decisive factor. At the present time mainly two types of phosphine ligands are used: those which are chiral at the phosphorus atom (P-chiral) and those which are chiral at the alkyl group of the phosphine (C-chiral). Monophosphine P-chiral ligands were used in the first studies, but the large number of stages in their synthesis and the need to resolve the racemic phosphine into enantiomers led to the wide use of C-chiral phosphines, which proved to be just as effective and which can be synthesised from readily available natural products.

This review represents an attempt at a systematic account of studies on the enantioselective hydrogenation reactions catalysed by homogeneous (and heterogeneous) metal complex catalysts containing transition metals and chiral ligands; the influence of the structure of the ligand on the optical yield is discussed. We may note that the reviews of studies in this field published previously[1-4] are extremely incomplete and are already obsolete.

Mention should be made of the principal definitions used in asymmetric catalysis. The efficiency of the asymmetric reaction is defined in terms of the optical yield (p, %):

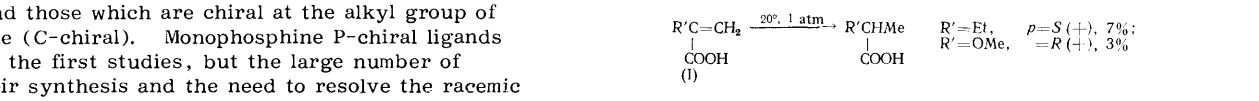
$$p = \{([R] - [S] / [R] + [S])\} \cdot 100$$

which represents the excess of one of the enantiomers in the product. The optical yield is determined experimentally from the ratio of the specific optical rotation of the reaction product to the specific optical rotation of the pure compound: $p = \{[\alpha]_{prod}/[\alpha]_{opt.pure\ comp.}\} \times 100$.

In this review the optically active product is characterised by the configuration, the sign of the optical rotation, and the optical yield; in terms of an abbreviated notation, we have, for example, $R(-)$, 25%. In a kinetically controlled process the optical yield does not vary with the degree of conversion; however, in practice p frequently changes in opposition to the overall specific rate of hydrogenation v and the efficiency of the enantioselective reaction can therefore be usefully characterised also by the rate of formation of the excess of one of the enantiomers w_R: $w_R = pv$ (mmol min^{-1}) per gramme of the catalyst.

II. CATALYSTS WITH P-CHIRAL LIGANDS

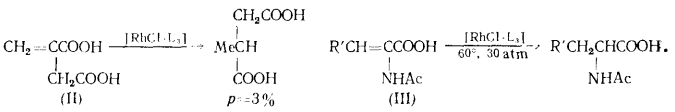
Enantioselective hydrogenation in the presence of Wilkinson's catalysts containing chiral phosphines was first achieved[5] in the hydrogenation of unsaturated acids in the presence of a rhodium complex containing the P*MePhR ligand with a chiral phosphorus atom P*:



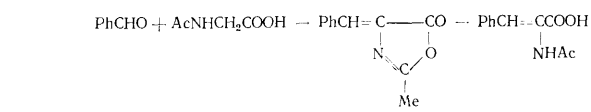
The catalyst was obtained *in situ* by mixing solutions of S(+)-P*MePh(n-Pr) and [Rh(hexa-1,5-diene)Cl]. The replacement of Et by MeO in the prochiral substrate reverses the sign of the enantioselectivity and leads to an R-product[6]. Presumably the methoxy-group is involved in coordination [as in the hydrogenation of methyl acetoacetate in the presence of the Ni-modified (+)-tartaric acid[7,8]], as a result of which the conformation of the immediate complex is inverted. In

the hydrogenation of α-substituted styrenes [PhC(R') = CH_2, R' = Et, Pr, iso-Pr, OEt, α-naphthyl, Br, or benzyl] in the presence of complexes containing other phosphines [P*MePhR, R = Pr, benzyl, iso-Bu, or t-Bu), a yield p = 12 to 14% was obtained[9].

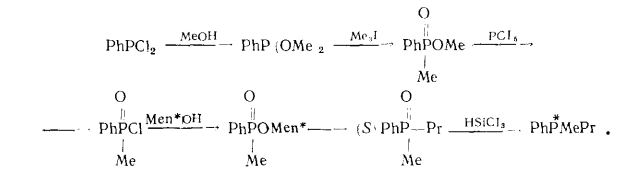
Almost simultaneously with the paper of Horner et al.[5], the communication of Knowles and Sabacky[10] was published, presenting data on the hydrogenation of atropic acid (I, R' = Ph) [p = (+), 15%] and itaconic acid (II):



The hydrogenation was carried out in a benzene–methanol mixture in a mixture of complexes containing the P*MePhR ligands, where R = Pr, iso-Pr, cyclohexyl, or *o*-anisyl. The complex with the ligand containing the *o*-anisyl group proved to be particularly effective: cyclohexyl-*o*-anisylmethylphosphine (CAMP) (here and henceforth the abbreviations adopted for ligands names in the original literature are employed). The complex is active in the hydrogenation of *N*-acylaminoacrylic acids (III), which can be readily obtained by the Erlenmeyer synthesis for substituted ligands via an intermediate azlactone, for example:



The optically active P-chiral monophosphine is synthesised in accordance with a mechanism involving a stage where the racemate is resolved into the enantiomers:

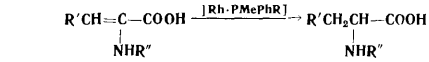


where Men* is the optically active methyl group. P*MePh-*o*-anisyl and P*Me-cyclohexyl-*o*-anisyl were obtained analogously. The complex is synthesised *in situ* by adding a solution of the ligand to the complex [RhCl(hexa-1,5-diene)]. All the hydrogenation reactions of the prochiral substrates are performed at 25 °C at a pressure of 2–3.5 atm in methanol with added NaOH. The results[11–13] are presented in Table 1. A patent[11] mentions also the possibility of using in this reaction the complexes of other metals (Ir, Ru, Os, Pd, and Pt) and the synthesis of optically active aminoacids (without indicating, however, the optical yields of the products).

The synthesis of optically active 3,4-dihydroxyphenylalanine (DOPA)—the preparation for the treatment of Parkinson's disease[13]. In relation to DOPA, asymmetric catalysis was first used for the industrial application of an asymmetric reaction in order to obtain a valuable product despite the difficulty of the preparation of the catalyst, which is the complex [Rh(hexa-1,5-diene)Cl.(+)P*MePh-*o*-anisyl], and the impossibility of regenerating it. The starting compound for the synthesis of L-DOPA was 4-acetoxy-*N*-acylamino-3-methoxycinnamic acid. A DOPA derivative was obtained with p = 60% and "pharmaceutically pure" DOPA was isolated from it after hydrolysis and recrystallisation. A DOPA derivative has been obtained with the yield p = 70.7% from *N*-acylamino-4-hydroxy-3-methoxycinnamic acid using the complex with P*Me-cyclohexyl-*o*-anisyl at 60 °C,[13] the addition of NEt_3 increasing p to 72%.

The high efficiency of rhodium (and also iridium and osmium) complexes with chiral diphosphine ligands in the hydrogenation of prochiral dehydroaminoacids and also α-(trifluoromethyl)vinyl acetate[14] has been reported[13]. Complexes having the general formula RR'P–CH_2–CH_2–PRR', where R = *o*-anisyl or ethoxyphenyl and R' = phenyl or tolyl, are obtained *in situ* from $[Rh(COD)Cl_2]BF_4$ (where COD = cyclo-octadiene) in methanol; the hydrogenation is carried out at 50 °C under a pressure of 4 atm. After recrystallising the products, the aminoacids phenylalanine (Phe), DOPA, and tryptophan (Trp) were obtained with optical yields of 92.8, 90.9, and 93.5% respectively.

Table 1. Hydrogenation of aminoacid precursors in the presence of rhodium catalysts with monophosphine ligands[10–13]:



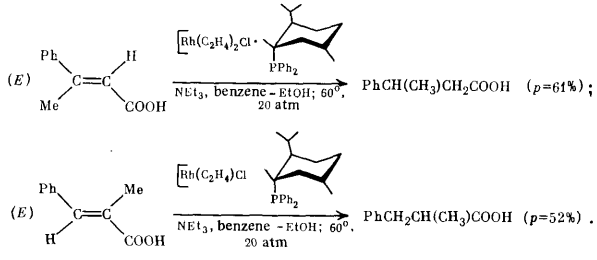
R	R'	R''	Product: amino-acid	Product: p, %
Pr	H	PhCO	Ala	6
o-Anisyl	H	PhCO	Ala	32
o-Anisyl	Ph	Ac	Phe	45
Pr	Ph	Ac	Phe	14.5
Pr	3-MeO-4-(OH)C_6H_3	Ac	DOPA	28
Cholesteryl	3-MeO-4-(OH)C_6H_3	Ac	DOPA	1.1
iso-Pr	3-MeO-4-(OH)C_6H_3	Ac	DOPA	20
Benzyl	3-MeO-4-(OH)C_6H_3	Ac	DOPA	8
m-Anisyl	3-MeO-4-(OH)C_6H_3	Ac	DOPA	0.1
o-Anisyl	3-MeO-4-(OH)C_6H_3	Ac	DOPA	46
o-Anisyl	3-MeO-4-Ac-C_6H_3	Ac	DOPA	50
Methylcyclohexyl-*o*-anisylphosphine*	3-MeO-4-(OH)C_6H_3	Ac	DOPA	70.7
Methylcyclohexyl-*o*-anisylphosphine**	3-MeO-4-(OH)C_6H_3	Ac	DOPA	65

* Ligand with 90% purity.

** Ligand with 80% purity.

III. CATALYSTS WITH C-CHIRAL LIGANDS

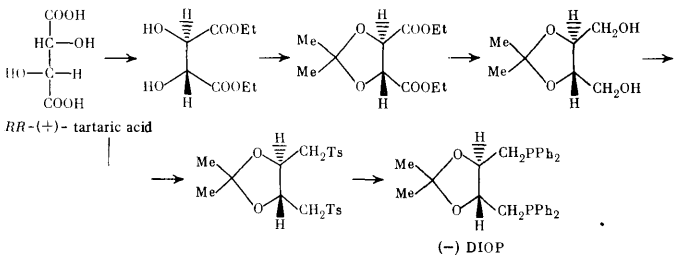
Catalysts of this type have come to be widely used. The first attempt to employ a complex containing a C-chiral ligand $PPh(CH_2C^*HCH_3C_2H_5)_2$, obtained from natural isopentyl alcohol, was unsuccessful[1]. Successful enantioselective hydrogenation was achieved[1,15,16] in 1971 using rhodium complexes with comparatively readily synthesised C-chiral ligands based on menthol; PPh_2Men (MDPP) and neomenthyldiphenylphosphine (NMDPP), the latter being more effective in the hydrogenation of compound (I, R = Ph) (p = 28%); other examples are given below:



The difference between the effects of complexes with these phosphines has been explained[1] by the fact that menthol and neomenthol are diastereoisomers with different properties and that the phosphines obtained from them exhibit different

capacities for coordination. MDPP apparently forms a more stable complex with rhodium than NMDPP, which is the reason for its lower efficiency.

A very effective and readily available diphosphine ligand (DIOP) was synthesised[17] from (+)-tartaric acid via the scheme



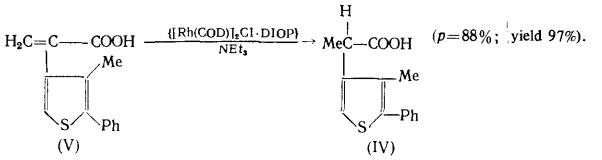
The comparative simplicity of the synthesis and the high enantioselectivity of the reaction of the complex containing DIOP attracted attention to this ligand and it became a common readily available reagent used in many preparative syntheses of optically active compounds.

The complex is obtained under conditions ruling out contact with air by adding a solution of the ligand mixed with NEt_3 to a benzene solution of $[RhCl(CoCt)_2]$ (CoCt = cyclooctene). The hydrogenation of prochiral compounds containing the C = C bond at room temperature and atmospheric pressure leads to the formation of products with very high optical yields. The following results were obtained already in the first study[17]: $p = 63\%$ for (I, R′ = Ph) and $p = 72\%$ for (III). With increase of the ratio P/Rh above two, the activity of the complex disappears as a consequence of the formation of the catalytically inactive complex $[Rh(DIOP)]^+Cl^-$. The complex [Rh-DIOP] is particularly active in the asymmetric synthesis of aminoacids by hydrogenating their precursors—substituted acrylic acids or their amides. The use of methyl esters or *N*-benzoyl derivatives as well as aliphatic acids reduces *p*, while the azlactone of *N*-acetamidocinnamic acid, benzoylhydanatoin, and dehydrobenzoylvaline are not hydrogenated at all.

The optical yields of the aminoacids obtained were enhanced further by recrystallising the products. Thus phenylalanine with $p = 88\%$ was obtained after a single crystallisation from crude *N*-acetylphenylalanine ($p = 72\%$); the overall yield was 66%. The catalyst based on (−)-DIOP leads to unnatural aminoacids of the D-series. In order to obtain the natural L-aminoacids, it is necessary to employ (+)-DIOP, which is synthesised from synthetic *SS*(−)-tartaric acid, which significantly reduces the practical value of the synthesis of aminoacids by this procedure. The chiral diarsine which is an analogue of DIOP makes it possible to obtain the natural aminoacid isomers but with low optical yields[18].

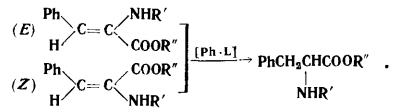
The DIOP ligand is a typical C-chiral diphosphine. The high enantioselectivity of the complex based on it can be accounted for by the configurational rigidity of the ligand molecule and the *trans*-position of the dioxolan ring relative to the chelate unit. This model of the complex explains satisfactorily its asymmetric activity[19]. The presence of the carboxy-group in compound (III) increases *p* under the influence of [Rh.DIOP], while the introduction of the ester group reduces the optical yield as a consequence of the weakening of the coordination of the substrate molecule. Bulky groups, for example adamantyl or bornyl groups, have a particularly marked effect[19].

The complex [Rh.DIOP] has been used in the synthesis of the anti-inflammatory compound (+)-(IV) by hydrogenating compound (V). Although compound (V) contains the sulphur atom of the thiophen ring, the hydrogenation proceeds smoothly and the optical yield is higher than in the hydrogenation of atropic acid [an analogoue of compound (V)], in the presence of this complex[20]:



The influence of the *E*,*Z*-isomerism of the substrate on enantioselectivity has been studied mainly in relation to the hydrogenation of substituted acrylic acids in the presence of rhodium complexes of DIOP[21] and bis(ethylidenephenylanisylphosphine) (EPAP).[14] Table 2 shows that there is a significant difference between the enantioselectivity of the hydrogenation of the *E*- and *Z*-isomers of *N*-acylaminoacrylic acids. Esterification of the acid in general reduces *p* for both *E*- and *Z*-isomers. The asymmetric hydrogenation of the latter is more effective than that of the *E*-isomers.

Table 2. Enantioselective hydrogenation of *E*,*Z*-isomers of acylaminocinnamic acids and their esters in the presence of rhodium complexes with the DIOP and EPAP ligands[14] [the optical yields (*p*,%) are quoted]:



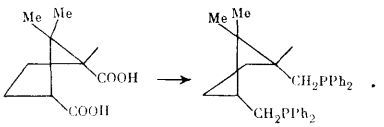
Substrate	R′	R″	Ligand DIOP	Ligand EPAP	Substrate	R′	R″	Ligand DIOP	Ligand EPAP
Z	Ac	H	81	94	*Z*	PhCO	Me	37.5	—
E	Ac	H	—	47	*Z*	PhCO	H	70	93
Z	Ac	Me	55	96	*E*	PhCO	H	25	39
E	Ac	Me	—	23	*E*	PhCO	Me	5.3	—

Table 3. Comparative catalytic efficiences of chiral rhodium complexes with various ligands in the enantioselective hydrogenation of prochiral *Z*- and *E*-substrates [the configurations and optical yields (*p*,%) of the corresponding products are quoted][124].

Substrate	Ligand Camphos	NMDPP	MDPP	CAMP	DIOP
Atropic acid	*S*; 6.1	*S*; 29.6	0	—	*S*; 44
(*E*) α-Methylcinnamic acid	*R*; 15.2	*R*; 60	*S*; 16.8	*R*; 12	*S*; 25
(*Z*) α-Methylcinnamic acid	*S*; 11.0	*R*; 25.2	0	*R*; 24	*R*; 33
(*E*) α-Phenylcinnamic acid	*S*; 11.8	*S*; 34.4	*R*; 27.2	*S*; 24	*R*; 15
(*Z*) α-Phenylcinnamic acid	*S*; 13.9	*S*; 9.1	*S*; 3.2	*R*; 1.5	*S*; 1
(*E*) β-Methylcinnamic acid	*S*; 9.7	*S*; 61.8	*S*; 1.2	*S*; 37	*R*; 14
(*Z*) β-Methylcinnamic acid	*R*; 11.4	*R*; 31.2	*S*; 30.6	*R*; 13	*S*; 28
Itaconic acid	*R*; 10.7	*R*; 8.1	*R*; 18.1	—	—
Mesaconic acid	*R*; 1.8	*R*; 5.9	*S*; 7.2	—	—

Table 3 shows that, when a monodentate molecule (α,β-unsaturated acids or esters) is hydrogenated, the influence of the *E*,*Z*-isomerism becomes less definite. The same picture has been observed also in hydrogenation in the presence of rhodium–amide catalysts[22,23] (see Table 10 below).

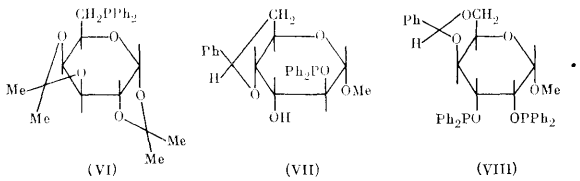
Table 3 presents comparative data on the catalytic efficiency of complexes with various ligands, including the diphosphine Camphos, obtained from (+)-camphoric acid[24]:



Thus interesting data have been obtained in the study of the simultaneous effect of the C- and P-chiral centres in the phosphine. Such a ligand was first used in the asymmetric dimerisation of olefins in the presence of the complex [NiP*Me-t-Bumen*]. The rhodium complex [Rh(COD)Cl. .P*MePhMen*], containing both the optically pure (i.e. C- and P-chiral) ligand(A) and the ligand(B) 87% epimerised at the P centre, has been used for hydrogenation[25]. The optical yields in the presence of the complexes with (A) and (B) were 13.5 and 27.5% for the *R*- and *S*-isomers in the hydrogenation of itaconic acid and 67.1 and 70.6% respectively for the *R*- and *S*-isomers in the hydrogenation of *E*-β-methylcinnamic acid. Apparently the presence of the ligands (A) and (B) in the catalytic complexes leads to enantiomeric products in both cases which indicates a significant influence of the P-chiral centre in the ligand of the rhodium complex on the stereochemistry of the products.

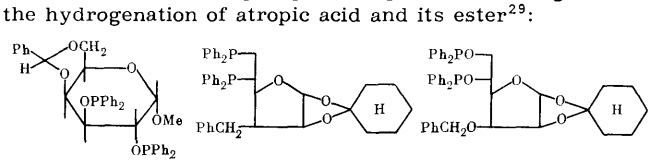
Rhodium complexes with chiral phosphinites (Camphinit) are also extremely effective catalysts[26]. A special comparison of the catalytic effect of the complexes [Rh.Camphos] and [Rh.Camphinit] demonstrated their similar enantioselectivities, the complex with phosphinite being more suitable for the hydrogenation of substrates without COOH or NHAc groups[26]. In this connection, the use of natural monosaccharides for the synthesis of both phosphines and phosphinites is extremely promising.

Ligands based on galactose (VI) and altrose (VII) have been synthesised[27]:

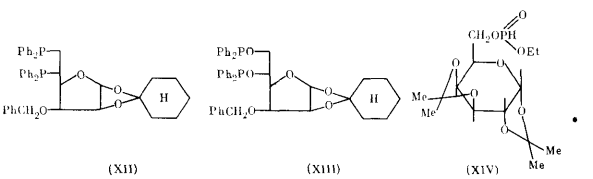


(VI) (VII) (VIII)

The catalyst was obtained *in situ* by the reaction of compound (VI) or (VII) with $[Rh(COD)Cl_2]_2$. The hydrogenation was carried out at 20 °C and atmospheric pressure. The hydrogenation of tiglic acid gave a higher optical yield (39%) than the hydrogenation of *N*-acetamidocinnamic and itaconic acids (1.7 and 2.7%). Catalysts containing diphosphonites based on glucopyranose (VIII) or galactopyranose (IX) are more effective[28]. In the presence of the complex of compound (VIII), *N*-acetamidocinnamic acid and its methyl ester give products with $p = 71$ and 60% respectively. Comparison of the enantioselectivities of the rhodium complexes of diphosphines and diphosphinites derived from glucofuranose [compounds (X) and (XI)] and idofuranose [compounds (XII) and (XIII)] demonstrated their similar efficiences in the hydrogenation of substituted acrylic acids; the enantioselectivity of the complexes with phosphinites proved to be higher in the hydrogenation of atropic acid and its ester[29]:

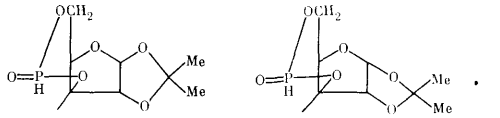


(IX) (X) (XI)



(XII) (XIII) (XIV)

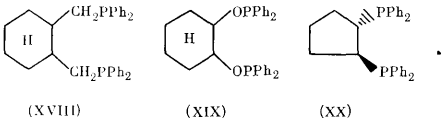
The chiral palladium complexes ($L_2PdCl_2PdL_2$), based on the acid galactose phosphite (XIV), also exhibit enantioselectivity in hydrogenation although it is weaker than that of the rhodium complexes. When compound (XIV) is treated with (−)-phenylethylamine, the derivative (XV) with a chiral P atom is formed and reacts with bis(π-palladium chloride) to produce a more effective complex. Palladium complexes with the cyclic phosphites (XVI) and (XVII) also exhibit an appreciable enantioselectivity[30–32].



(XVI) (XVII)

The efficiency of this palladium complex in the hydrogenation of citraconic acid is noteworthy, while in the presence of rhodium complexes with a wide variety of ligands the acid cannot by hydrogenated enantioselectively[1].

Cyclic diphosphines and diphosphinites (XVIII)–(XX) have also been used to synthesise rhodium complexes:



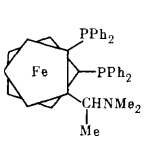
(XVIII) (XIX) (XX)

Table 4. Comparison of the enantioselectivities of rhodium complexes with the ligands (XIX), (XX), and DIOP in the hydrogenation of prochiral unsaturated compounds [the configurations and optical yields (p,%)] are quoted[35].

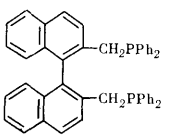
Substrate	*t*, °C	Ligand		
		(XIX)	(XX)	DIOP
α-Ethylstyrene	50	*R*; 33	*R*; 60	*S*; 24.5
cis-2-Phenylbut-2-ene	50	*S*; 14.4	—	—
Atropic acid	50	*S*; 0.7	0	*S*; 6.3
Methyl atropate	50	*S*; 4.5	*S*; 20	*R*; 7
N-Acetamidocinnamic acid	0	*S*; 68.5	*S*; 12	*R*; 63
Methyl-*N*-acetamidocinnamate	50	—	*S*; 43	*R*; 55
N-Acetamidoacrylic acid	−20	*S*; 78.5	0	*R*; 73
N-Acetamido-*p*-hydroxycinnamic acid	50	*S*; 48.5	—	—

The compound *trans*-(+) (XIX) and the complex [RhCl(hexa-1,5-diene)$_2$] form a chelate which has a rigid structure and in its presence the enantioselective hydrogenation of prochiral precursors of aminoacids proceeds with an extremely high efficiency[34]. The contraction of the ring and the binding of $P(Ph_3)$ groups directly to the ring increase the enantioselectivity of the complex [ligand-(+)-*trans*-(XX)].[35] Even the hydrogenation of α-ethylstyrene, which has no polar groups, proceeds with a high efficiency in this instance. In the hydrogenation of unsaturated acids the yield p is low, but it increases somewhat in the hydrogenation of the esters. Table 4 presents the values of p obtained using complexes with the ligands (XIX) and (XX) and for comparison also with DIOP.

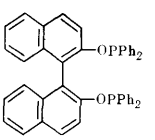
Isomeric atropisomericphosphines constitute another type of chiral ligands. The ferrocenyl derivatives of mono- or diphosphines, which exhibit simultaneously planar and central chirality of type (XXI), have been used in a complex with [RhCl(hexa-1,5-diene)] in the hydrogenation of acetamidocinnamic acids. The complexes (particularly the cationic complex) exhibit a very high enantioselectivity in the synthesis of the most important aminoacids—phenylalanine, tyrosine, and DOPA. The optical yield depends greatly on the polarity of the medium and on the presence of the NMe_2 group in the ligand[36] (Table 5). Tamao et al.[37] were the first to use the atropisomeric ligands (XXII) and (XXIII). The complex with compound (XXIII) proved to be more effective, the aminoacid esters and not the free aminoacids being formed in a high optical yield[38]:



(XXI)

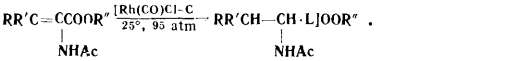


(XXII)



(XXIII)

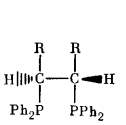
Table 5. Hydrogenation of acylacrylic acids in the presence of rhodium catalysts with atropisomeric ligands[36]:



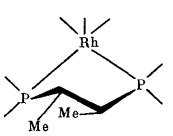
R	R'	R''	Ligand	Product	p, %	Solvent
H	Ph	H	(XXIII)	Phe	9	—
H	Ph	Me	(XXIII)	MePhe	76	—
H	H	H	(XXIII)	Ala	6	—
H	H	Me	(XXIII)	MeAla	76	—
Ph	Me	Et	(XXIII)	ethyl β-methylcinnamate	44	—
H	Ph	H	(XXI)	Phe	93	MeOH
H	Ph	H	(XXI)	Phe	92	EtOH—H_2O
H	Ph	H	(XXI)	Phe	89	MeOH—H_2O
H	4-$AcOC_6H_4$	H	(XXI)	Tyr	8	MeOH
H	4-$AcOC_6H_4$	H	(XXI)	Tyr	38	EtOH
H	4-$AcOC_6H_4$	H	(XXI)	Tyr	87	MeOH—H_2O
H	3-MeO-4-$AcOC_6H_3$	H	(XXI)	DOPA	36	EtOH
H	3-MeO-4-AcO-C_6H_3	H	(XXI)	DOPA	86	MeOH—H_2O
H	3,4-$(CH_2O_2)C_6H_3$	H	(XXI)	DOPA	52	MeOH—H_2O

* The NHAc group in the initial substrate has been replaced by H.

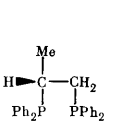
A highly effective complex is formed also when[39] the five-membered chelate ring, formed, for example, from ligand (XXIV), has a fixed conformation[39] with two asymmetric carbon atoms and equatorial methyl groups [compound (XXV)]. The cationic complex $[Rh.(XXV)]^+.ClO_4^-$ (XXVI) also exhibits a high enantioselectivity. However, it has been shown[39] that the complex with the ligand (XXVII), having a single asymmetric carbon atom, is no less effective. The most typical results, using the complex [Rh.(XXIV)] (Chiraphos) in the hydrogenation of substituted aminoacrylic acids, are presented in Table 6.



(XXIV)



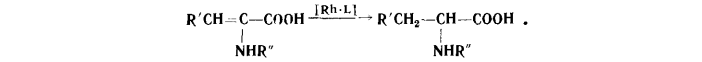
(XXV)



(XXVII)

It is seen that the complex exhibits an exceptionally high enantioselectivity in the case of aminoacids, leucine and phenylalanine having been obtained with $p = 100\%$. The disadvantages of the method include the necessity to synthesise the ligand from S(+)-lactic acid, which is difficult to obtain in a pure form. King et al.[40] attempted to eliminate this disadvantage and synthesised compound (XXII, R = Ph) from the enantiomers of mandelic acid.

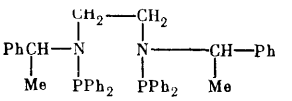
Table 6. Enantioselective hydrogenation in the presence of the complex [Rh.Chiraphos] [the optical yields (p, %) are quoted][39,40]:



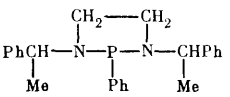
Substrate	R'	R''	Aminoacid product	Solvent	
				THF	EtOH
Z	H	Ac	AcAla	88	91
Z	Ph	Bz	BzPhe	99	95
Z	Ph	Bz	BzPhe	83	—
Z	Ph	Ac	AcPhe	74	89
Z	iso-Pr	Ac	AcLeu	100	93
Z	HOC_6H_4	Bz	BzTyr	92	—
E	HOC_6H_4	Bz	BzTyr	80	88
Z	4-AcO-3-$MeOC_6H_3$	Ac	DOPA	80	83
—	Ph	Ac	AcPhe *	82	—
—	Ph	Bz	BzPhe *	86	—

* L = (XXIV), R = Ph; in the remaining cases R = Me.

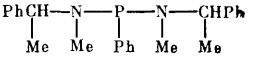
Morrison and Masler[16] were the first to report an attempt to employ chiral aminophosphines. A series of diaminodiphosphines have been synthesised[41] using S-α-phenylethylamine and the high efficiency of complexes with the ligands (XXVIII)-(XXX) has been demonstrated:



(XXVIII)



(XXIX)

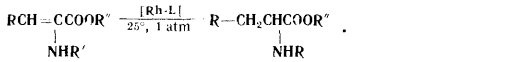


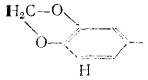
(XXX)

The catalyst was obtained *in situ* by the reaction of [RhCl.$(CH_2=CH_2)]_2$ with compound (XXVI). Although the chiral centre in the ligand is remote from the reaction centre, the efficiency of the catalyst proved to be extremely high and comparable to that of [Rh.DIOP], the data for which are presented in brackets in Table 7.[41] The high efficiency of the complex with ligand (XXVIII), particularly when a polar solvent is used, has been explained[42] by the ionisation of the complex and the formation of a hydrogen bond between the solvent and substrate molecules. This has been confirmed by the finding that the cationic complex $[RhL_2(Solv)].BF_4$ is still more active than the chlororhodium complex; aminoacids are formed with $p = 82.5\%$. A high yield can be achieved both by the coordination of the polar groups in the substrate to the metal and by the interaction of the substrate with the ligand containing functional groups other than the

phosphine group. This has been shown in the hydrogenation of itaconic acid for which complexes containing chiral phosphines have been in general not particularly effective, although in certain cases the optical yield reached 53%.[20]

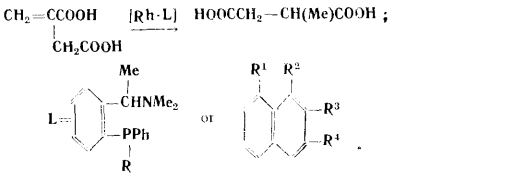
Table 7. Enantioselective hydrogenation in the presence of complexes containing aminophosphine ligands [the configurations and optical yields (p,%) of products are quoted][41]:



R	R′	R″	Configuration; p,%	Ligand
H	Ac	H	*R*; 73 (73)	(XXVIII)
Ph	Ac	H	*R*; 84 (82)	(XXVIII)
Ph	Ac	H	82.5	(XXVIII)
Ph	Ac	Me	*R*; 49 (55)	(XXVIII)
Ph	Bz			
	Ac	H	*R*; 68 (64)	(XXVIII)
		H	*R*; 75 (79)	(XXVIII)
H	Ac	H	*S*; 7.5	(XXIX)
Ph	Ac	H	0	(XXIX)
Ph	Ac	H	*R*; 19.7	(XXX)

The influence of the structures of a series of aminophosphine complexes of rhodium has been studied[43]. The results presented in Table 8 have been obtained under comparable conditions for the ratio L/Rh = 2.

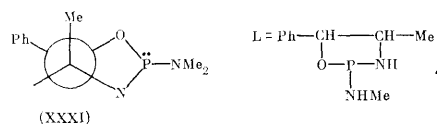
Table 8. Enantioselective hydrogenation in the presence of rhodium complexes containing aminophosphine ligands [the configurations and optical yields (p,%) of products are quoted][43]:



Ligand						Neutral complex	Cationic complex
configuration	R	R^1	R^2	R^3	R^4		
S	Ph	—	—	—	—	*R*; 18	*R*; 18
SS	Bu	—	—	—	—	*S*; 20	*S*; 17
S	—	H	$CHMeNMe_2$	PPh_2	H	*R*; 41	*R*; 43
—	—	PPh_2	$CHMeNMe_2$	H	H	*S*; 20	—
R	—	H	PPh_2	$CHMeNMe_2$	H	*S*; 5	0
R	—	H	H	$CHMeNMe_2$	PPh_2	*S*; 3.5	*S*; 15

The maximum yield was obtained in the presence of a complex with ligand (XXX), whose effect is comparable to that of [Rh.DIOP]. The introduction of a chiral P centre into the ligand [the aminophosphine (XXIX)] leads to the inversion of the configuration of the product, which occurs also when the H atom in the amino-group is replaced by Me, for example in the diphosphine derivative 1,2-bis(diphenylphosphinoamino)cyclohexane[45]. The replacement of the chiral α-phenylethyl group in compound (XXVIII) by the pinanyl group reduces the enantioselectivity of the catalyst[44]. The monoaminophosphines (XXIX) and (XXX) are less effective than the diphosphines. An attempt has been made[42] to repeat the results of Florini et al.[41] who used the ligands (XXIX) and (XXX). Despite the data of Florini et al.[41], the effect of the complex with compound (XXIX) could not be reproduced[42].

The derivatives of oxazaphospholan (XXXI) have been synthesised from (−)-ephedrine and used as ligands in palladium complexes of the following type[46]:

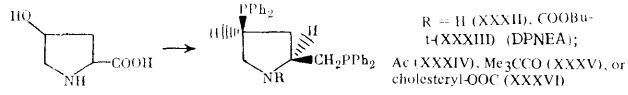


(XXXI)

The presence of chiral C and P centres in ligand (XXXI) was established by circular dichroism[46]. The hydrogenation of *N*-acetamidocinnamic acid, its azalactone and dimethyl itaconate took place with yields of 16.4, 4.0, and 9.9% respectively. The complex is one of the few chiral palladium complexes capable of effecting asymmetric hydrogenation. The low optical yield in the reaction is apparently associated with the partial decomposition of the complexes in the reaction.

A new synthesis of a chiral rhodium complex involving the substitution of one ligand in the coordination sphere of the triphenylphosphine complex by chiral α-phenylethylamine has been achieved[47]. The complex exhibits enantioselectivity in the hydrogenation of *N*-acetamidocinnamic acid (p = 20.2%) and its methyl ester (p = 11.8%). The optical yield increases with increase of the ratio amine/$RhCl(PPh_3)_3$ to a definite limit.

Ligands having two phosphine groups and the NH and NR groups have been obtained[48] from hydroxyproline[48]:



The catalyst was obtained *in situ* by the interaction of the ligand with the complex [Rh.hexa-1,5-diene]Cl; its efficiency was investigated in the hydrogenation of substituted aminocinnamic acids; the complex with compound (XXXIII) is more effective than that with (XXXII). NEt_3 influences the optical yield for complexes with a substituted NH-group, whereas in the case of [Rh.(XXXII)] this influence is absent as a consequence of the interaction of the free NH group in the ligand with the COO group in the substrate molecule. The [Rh.(XXXIII).NEt_3] system exhibits a greater enantioselectivity (p = 80–90%) when the reaction is carried out in ethanol than in methanol or water, which indicates the more effective interaction of the complex with the substrate in a less polar solvent[48]. Other substrates normally employed yielded the following results: p = 15 and 24% were obtained for (Z)-α-methylcinnamic acid and dimethyl itaconate in the presence of [Rh.(XXXIII)], and p = 29.5% was obtained in the presence of [Rh.(XXXVI)].[49] In addition, hydrogenation of olefins in the presence of the last complex yielded hydrocarbons:

$$CH_2=C(Et)R \rightarrow MeCH(Et)R$$

R = n-Bu, p=5.8 %, R=Ph, p=24.7%

If the NH-group of the ligand is acylated [compounds (XXXIV) and (XXXV)], the addition of Et_3N impairs the enantioselectivity and can actually lead to a configuration of the product which is the opposite to that obtained in the presence of the complexes with compounds (XXXII) and (XXXIV) (Table 9)[50]. The activity of the complexes of compounds (XXXIV) and (XXXV) in the hydrogenation of benzyl derivatives of the alanine precursor, which is of great interest for peptide synthesis, has been studied[50].

Table 9. Hydrogenation of acylacrylic acids in the presence of rhodium complexes containing heterocyclic diphosphines(L): [50]

$$RCH{=}CCOOR' \xrightarrow{[Rh\cdot L]} R{-}CH_2{-}CHCOOR'$$
$$\quad\;\; NHR'' \qquad\qquad\quad NHR''$$

R	R'	R''	Configuration of product; p, %	L	Solvent
Ph	H	Ac	S; 6	XXXII	ethanol
Ph	H	Ac	R; 30	XXXIII	methanol
Ph	H	Ac	R; 91	XXXIII	ethanol + NEt_3
Ph	Me	Ac	S; 7	XXXIII	ethanol
Ph	Me	Ac	R; 15	XXXIII	ethanol + NEt_3
3,4-$CH_2O_2C_6H_3$	H	Ac	R; 83	XXXIII	ethanol + NEt_3
3,4-$CH_2O_2C_6H_3$	H	Ac	R; 32	XXXIII	ethanol
3-MeO-4-$AcOC_6H_3$	H	Ac	R; 86	XXXIII	ethanol + NEt_3
4-$AcOC_6H_4$	H	Ac	R; 87	XXXIII	ethanol + NEt_3
H	H	$PhCH_2COO$	R; 57	XXXIV	ethanol
H	H	—	S; 8	XXXIV	ethanol + NEt_3

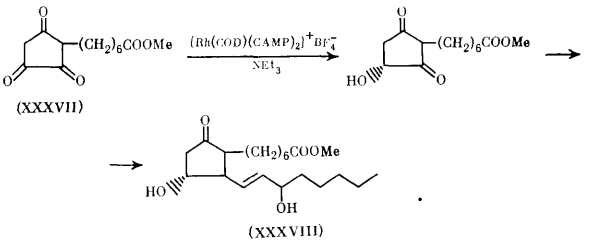
The efficiences of [Rh.(XXXIII)] and other rhodium-phosphine complexes have been compared in the hydrogenation of itaconic acid[51]. At 20 °C and a pressure of 20 atm in the presence of the complex [Rh.(XXXIII)]with added NEt_3, methylsuccinic acid was obtained with $p = 92\%$. This high optical yield was achieved after converting the complex into the cationic form $[L.Rh(COD)]^+ClO_4^-$ † with the ratio NEt_3 : itaconic acid = 1. For the neutral complex, p increases from 78.8 to 90.6% with increase of this ratio, i.e. in fact when the complex is converted into the cationic form. Thus the role of NEt_3 reduces to activating the carbonyl substrate and the formation of the carboxylate anion, which then interacts with rhodium in the coordination sphere of the complex and is converted into a cationic complex[51]. Comparative hydrogenation of itaconic acid in the presence of a number of complexes showed that, in the series of the chiral ligands PMePhPr-n,[10] NMDPP,[1] MDPP,[1] Camphos[20], PMePhMen,[25] DIOP,[16] BPPA,[43] Amphos[43], and DPNEA [48,51] the last proved to be the most effective; the optical yield reaches 92% in the presence of the complex with the ligand (XXXIII) (DPNEA).

The enantioselective hydrogenation of the C = O and C = N bonds has been less well studied than the hydrogenation of the C = C bond. Wilkinson's catalyst is known to be relatively inactive in the hydrogenation of the C = O bond and also it induces the decarbonylation of aldehydes. However, the use of cationic rhodium complexes with phosphine ligands made it possible to achieve the hydrogenation of certain ketones and Bonvicini et al.[52] reduced ketones for the first time under the influence of the rhodium complex with the P-chiral ligand $PMePhCH_2Ph$ (the PMePhEt ligand proved to be relatively ineffective according to Tanaka et al.[53] owing to the small difference between the bulks of the phosphine groups). The reaction was performed at 20 °C and atmospheric pressure in anhydrous ethanol[52]. The catalyst is in general relatively inactive and the overall rate of reaction decreases in the course of the hydrogenation. Phenylbutanol ($p = 8.6\%$) and 2-butanol ($p = 1.9\%$) were obtained from the corresponding ketones. The optical yields are small but are comparable to those obtained in the presence of the same complex in the hydrogenation of prochiral C = C substrates[6]. The introduction of DIOP into the complex in place of the P-chiral phosphine permits the enantioselective hydrogenation not only of the C = O but also of the C = N bond[54].

The use of the cationic rhodium (and also iridium) complex[55] $[Rh(COD)(CAMP)_2]^+BF_4^-$ with the CAMP ligand in the hydrogenation of ketones at 75 °C and 6 atm in isobutyric acid solution with added 0.1% of water is much more effective[10]: the ketones MeCOR (R = ET, Hex, iso-Bu, Bz, or Ph_2CH) give rise to alcohols with optical yields of 12, 14, 14, 19, and 32% respectively. The antiparallel variation of p and of the overall rate of reaction has been observed[55]. Methyl acetoacetate reacts much faster than ketones in alcohol (25°, 34 atm) with formation of methyl β-hydroxybutyrate ($p = 56\%$). The yield p is greatly influenced by the hydrogen pressure, temperature, the added water, and the nature of the solvent. It has been shown for the hydrogenation of 2-octanone (75 °C, 6 atm) that p increases from 0.3 to 12% in the series of solvents tetrahydrofuran (THF) < ethyl acetate < dimethylacetic acid < acetic acid. When the reaction is carried out in isobutyric acid, an increase of the water content in the solvent to 8% reduces sharply the optical yield (from 10–14 to 5%).[55]

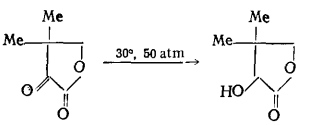
The complex (Rh(norbornadiene).(XXVIII)] is able to catalyse the hydrogenation of ketones (25°, 12 atm): the corresponding alcohols were obtained with $p = 17$ and 8% respectively from acetophenone and hexyl methyl ketone[41]. The complex [Rh(XX)] exhibits an appreciable enantioselectivity[35]. The hydrogenation of acetophenone at 80 °C leads to the corresponding alcohol with $p = 22\%$, while that of propiophenone gives rise to the alcohol with $p = 3.5\%$. The enantioselective dehydrogenation of the racemic α-phenylethyl alcohol takes place in the presence of the complex $[RuCl_2 \cdot PPh_3 \cdot (neomenthylPPH_2)]$. From this it follows that a rigorous determination of the degree of asymmetric synthesis in each individual case requires a detailed study in order to be able to show that the enantioselective reaction does not occur.

The hydrogenation of the intermediate (XXXVII) in the synthesis of prostaglandin (XXXVIII), which is a reaction of practical importance, has been achieved[56] in the presence of the complex [Rh.CAMP] ($p = 68\%$):



(XXXVII) (XXXVIII)

The complexes of the ligands (XXXIII) and (XXXVI) are capable of hydrogenating enantioselectively the keto-group in the pyruvates MeCOCOOEt and MeCOCOOBu-n with $p = 62$–65%.[49] Ketopanthoyl-lactone is hydrogenated to R(−)-panthoyl-lactone (XXXIX) with a high optical yield ($p = 86.7\%$).[57]

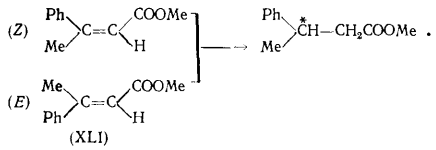


(XXXIX)

† COD = 1,5-cyclo-octadiene (Ed. of Translation).

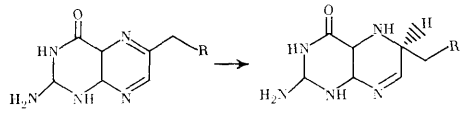
IV. RHODIUM AND PALLADIUM CATALYSTS CONTAINING AMIDES AND AMINES

Chiral rhodium-amide catalysts, capable of the enantioselective hydrogenation of unsaturated acids[22,23] as well as acetamidoacrylic acid[58], are obtained *in situ* when $[(Py)_3.RhCl]$ is treated with $NaBH_4$ in a solution of an optically active amide. With decrease of the concentration of the chiral amide to 5% in solution in the methyl ether of diethylene glycol, the enantioselectivity of the catalyst is preserved, which shows that, instead of the solvation of the complex by the chiral solvent, the chiral (apparently ionic) complex $[(Py)_2(amide)RhCl(BH_4)]^+Cl^-$ (XL) is formed. Various amides have been investigated as ligands (Table 10). The interesting fact (see Table 10, Nos.7–10) that the *Z,E*-isomerism of the substrate has almost no influence in this instance on the enantioselectivity is striking[22]



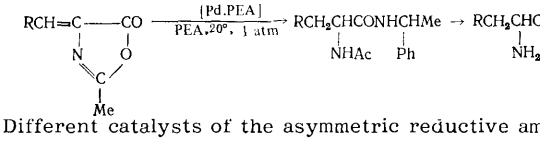
(XLI)

Apart from this model reaction involving the hydrogenation of compound (XLI), the application of the complex with the amide (XL) made it possible to hydrogenate the C = C bond in the precursor of the aminoacid (III, R = Ph) and to obtained acetylphenylalanine with $p = 75.3\%$ and an overall yield of 66%.[56] Another example of a reaction of practical importance is the synthesis[59] of folic acid (XLII) under the influence of the rhodium complex containing α-phenylethylformamide as the chiral ligand, via the reaction:

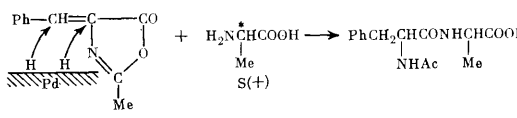


(XLII)

In the presence of palladium- or rhodium-based metal complex catalysts incorporating α-phenylethylamine (PEA), enantioselective reductive aminolysis of the azlactones of substituted acylaminoacrylic acids take place with formation of the corresponding aminoacid amides and, after their hydrolysis, of the aminoacids[60]:



Different catalysts of the asymmetric reductive aminolysis of azlactones have been obtained by the reduction of $PdCl_2$ or $RhCl_3$ in aprotic solvents containing *S*(−)-PEA, H_2, $NaBH_4$, and *S*(−)-α-phenylethylaminoborane have been used as the reductants[60]. In *trans*-$Pd(PEA)_2Cl_2$-*S*(−)-α-phenylethylaminoborane system the excess of the *SS*-amide formed on reduction was 53%. An important component of the catalytic system is the chiral nucleophile, which can be PEA or S-alanine. In the latter case the reaction leads to the formation of a dipeptide, which is of considerable practical interest because dipeptides are assimilated by organisms more readily than aminoacids:



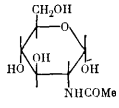
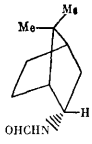
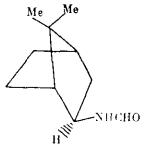
V. CHIRAL COBALT HYDROGENATION CATALYSTS

The development of effective chiral hydrogenation catalysts without platinum metals is of special interest. Cobalt complexes are extremely active dissymmetric catalysts capable of hydrogenating both C = C and C = O bonds. Two types of catalysts are known. They are based on $Co(CN)_5$ or $Co(DMG)_2$ (where DMG = dimethylglyoxime) and contain chiral ligands. The complex with $Co(CN)_5$, containing coordinated isoleucine as the aminoacid L, exhibited a weak enantioselectivity ($p \cong 0.1\%$) in the hydrogenation of atropic acid (I, R = Ph).[62] The replacement of the coordinated aminoacid by *R*(−)-propylenediamine increases *p* to 1.1%, while the introduction of *S*(+)-*N,N'*-dimethylpropylenediamine makes it possible to obtain a product with $p = 7.1\%$ from (I, R = Ph). The low enantioselectivity is apparently associated[63] with the difficulty of achieving the coordination of the substrate in the complex. It has been noted that amines with opposite configurations lead to the same *S*-acids.[64,65]

Table 10. Enantioselective hydrogenation of *E*- and *Z*-methyl β-methylcinnamates in the presence of rhodium—amide catalysts[22,23]:



(*Z*) (*E*)

№	Ligand: formula	optical purity	Substrate (XLI)	Configuration of product; *p*, %
1	$PhCH(Me)CH_2NHCHO$	100	*E*	*S*; 57
2	ditto	96	*E*	*R*; 48
3	ditto	100	*E*	*S*; 55
4	$(PhCH(Me)NHCO)_2$	—	*E*	*S*; 45
5	$MeCH(OH)CONH_2$	92	*E*	*R*; 16
6		99	*E*	*R*; 14
7		96	*Z*	*S*; 45
8	ditto	96	*E*	*S*; 40
9		100	*Z*	*S*; 28
10	ditto	100	*E*	*S*; 22

It is known that the complex $[Co(DMG)_2.amine]$ is active in the hydrogenation of the carbonyl group and azo-, azoxy-, and nitro-groups. A high enantioselectivity in the hydrogenation of the C = O bond has been observed for this complex after the introduction into its composition of a chiral

aminoalcohol or amine. Thus [Co(DMG)$_2$.quinine] exhibited a high enantioselectivity in the hydrogenation of benzil[66]:

$$\underset{S(+)\text{-benzoin}\quad p=61.5\%}{\text{PhCO—COPh} \rightarrow \text{PhCH(OH)COPh}};$$

The reaction proceeds under mild conditions (room temperature and atmospheric pressure). The ratio substrate/Co = 10–20, quinine/Co = 2, and the solvent is benzene or THF. In a polar solvent p decreases. Under the reaction conditions, enantioselective separation of the racemic benzoin does not occur and the chirality of the product therefore rises at the catalytic stage[66].

The hydrogenation of the ketones of the type PhCOCOR also leads to $S(+)$-benzoins. Since the product readily racemises, the true value of p was found by extrapolating the time variation of p to the time $\tau = 0$. The hydrogenation of diacetyl and ethylphenyl glyoxylate is accompanied by reductive dimerisation, which also leads to chiral products; this shows that the intermediate chiral complex reacts with the second substrate molecule without the dissociation of the Co–C bond[67]. The results are presented in Table 11.

Table 11. Enantioselective hydrogenation of α-diketones and α-ketoesters in the presence of the complex [Co(DMG)$_2$. .quinine][67].

Substrate	t, °C	Product			
		formula	yield, %	$[\alpha]_D$	p, %
PhCOCOPh *	−10	PhCH(OH)COPh	95	(+)0.86	*S*; 73
PhCOCOMe	20	PhCH(OH)COMe	88	(+)0.88	*S*; 56
MeCOCOMe	30	MeCH(OH)COMe	—	(−)0.2	*R*; 2.5
MeCOCOMe	20	MeCH(OH)COMe	54	(−)2.44	*R*; 30
PhCOCOOEt	30	PhCH(OH)COOEt	32	(+)0.28	*S*; 13.7
PhCOCOOPr-iso	—	PhCH(OH)COOPr-iso	62	(+)0.18	*S*; 11.5

* The reaction was carried out in toluene and in the remaining cases in the absence of a solvent.

The introduction of various chiral amines and aminoalcohols into the complex as ligands showed that the configuration of benzoin formed on hydrogenation of benzil is determined by the coordination of the C*–NH$_2$ and C*–OH centres in the ligand molecule: one amino-group is insufficient for enantioselective hydrogenation. For example, when brucine, O-acetylquinine, or α-phenylethylamine is introduced into the complex, the latter is incapable of effecting the enantioselective reaction, while the introduction of quinine, quinidine, or cinchonidine is approximately equally effective ($p \cong 33\%$). In the sequence *N*-methylephedrine > ephedrine > ψ-ephedrine the yield p decreases from 28 to 7.8%. These data indicate the diminution of the efficiency of the catalyst for the threo-disposition of the amino- and hydroxy-groups in the ligand[68]. The introduction of an additional amine (or triphenylphosphine) into the complex as well as the decrease of the reaction temperature to −10 °C made it possible to increase p to 78%. The base is then coordinated in the axial position, displacing the chiral aminoalcohol. The use of the aminoalcohol hydrochloride increases p, while the increase of the basicity of the amine greatly reduces p (Table 12). It has been suggested[69] that the chiral aminoalcohol is not linked directly to the complex Co(DMG)$_2$ and the entire complex thus resembles an oxidoreductase enzyme in which the catalytic and specific centres are separated. In this case the chiral aminoalcohol corresponds to the apoenzyme. The independence of p of the overall rate of the reaction, which can increase by an order of magnitude while p remains unaltered, is regarded as confirmation of this view[69]. However, one should note that this conclusion by the authors is not entirely convincing, since the reaction kinetics were not investigated and the process was inferred from the initial velocity.

Table 12. The influence of the amine (B) introduced into the complex [Co(DMG)$_2$.Q] on the optical yield and rate of hydrogenation of benzil[68,69].

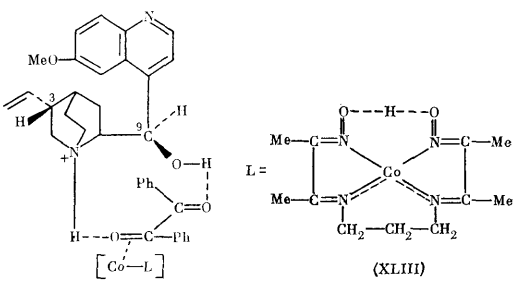
Q	B	B/Co	Q/Co	Q·HCl/Co	p, %	v *
Quinidine	Benzylamine	1	1	0	*R*; 48	6.0
Quinidine	Benzylamine	1	3	0	*R*; 51	12.0
Quinine	—	0	1	1	*R*; 61.5	1.5
Quinine	Benzylamine	1	0	1	*S*; 59	6.5
Quinine	Benzylamine	1	1	1	*S*; 61	13.6
Quinine	Triphenylphosphine	1	1	1	*S*; 61.5	0.3

* v is the rate of reaction expressed in millimoles of absorbed hydrogen per second per mole of catalyst.

If the hydrogenation is carried out at the interface in such a way that the benzene layer contains the substrate and quinine and the aqueous layer consists of a solution of the complex containing the amine (ammonia or aminoacid), then the course of the asymmetric reaction shows that the aminoalcohol does not enter directly into the cobalt complex. The chiral agent can be either in the benzene layer (quinine) or in the aqueous layer (ascorbic acid, aminoacid)[70].

This unusual mechanism of the reaction involving chiral cobalt complexes has been investigated for the chelate[71,72] formed *in situ* from compound (XLIII), quinine, and benzylamine in solution in a propanol-toluene mixture.

Scheme 1



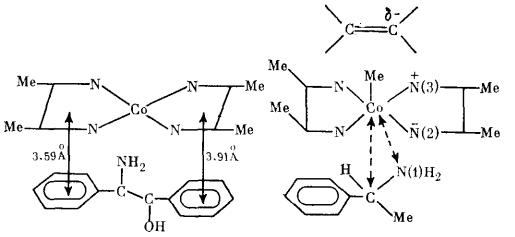
(XLIII)

The hydrogenation was carried out below −8 °C for 24 h. The products of the reactions involving methyl benzoylformate, benzoin, and methylpyruvate were obtained in yields of up to 48, 79, and 48% respectively.

A reaction mechanism, postulating the simultaneous coordination of the substrate, quinine, and hydrogen molecules to a single catalytic centre, was put forward[72] on the basis of the results of a number of studies[63–69]. This unusual mechanism is based on the hypothesis that the chiral centre in the ligand (quinine) is linked to the substrate and not to the metal (Scheme 1). In this connection it was of interest to investigate the influence of the chiral C(3) and C(9) centres on the enantioselectivity by replacing quinine by its

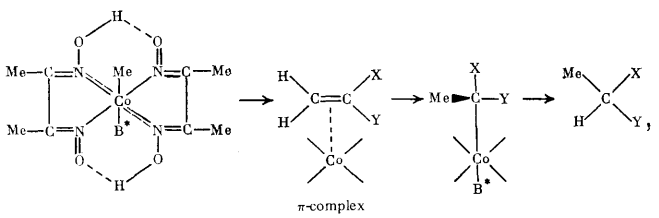
derivative and by diastereoisomers. This situation resembles that of enzyme systems where the centre determining the stereochemistry of the reaction is remote from the catalytically active centre. The observed independence of p of the overall rate of reaction can be understood in terms of this mechanism.

X-Ray diffraction analysis of a model compound—the complex (XLIV) having an analogous structure[73]—showed that N(1) and O(1) are in the *trans*-positions but the OH group in the chiral aminoalcohol is remote from $Co(DMG)_2$ and does not form a hydrogen bond with it: coordination takes place via the amino-group.



(XLIV) (XLV)

A more detailed study of the structure of the complex was performed on the model compound (XLV).[73] α-Phenylethylamine was used as the chiral amine, but one should note that this complex has no chiral catalytic properties. It contains the methyl group, which distinguishes it from the enantioselective catalytic complex, but it was assumed[73] that the methyl group does not influence the properties of the complex. Nor is it clear how hydrogen is activated in such a complex. The study of this model established that the introduction of a chiral amine into the complex [Me.(α-phenylethylamine).$Co(DMG)_2$] results in the deformation of the plane of the $Co(DMG)_2$ molecule. The strong repulsion between the amine and $Co(DMG)_2$ causes a shift of the N(1) atom towards N(2) and the  plane is then distorted. The polarisation of the N(2) and N(3) atoms in $Co(DMG)_2$ causes the orientation of the prochiral olefin. A mechanism of the hydrogenation of the C = C bond via the formation of π- and σ-complexes was proposed on the basis of a study of the structure of the complex (XLV)[73]:



where B* is the optically active base.

Catalytically active systems of the type of Ziegler–Natta catalysts based on cobalt, namely [$Co(acac)_2$.$AlEt_3$.$P(Ph)_2$-(neomenthyl)] and [$Co(L\text{-}I\ leu)_2$.$AlEt_3$], also exhibit enantioselectivity in the hydrogenation of isomeric 2-phenylbutanes: the optical yields of 2-phenylbutane were 5.4 and 25% respectively[74].

VI. HETEROGENEOUS METAL COMPLEX CATALYSTS LINKED TO A POLYMERIC CHIRAL LIGAND

It is evident that metal complex catalysts linked to a polymeric carrier have many advantages over their soluble analogues. These are mainly the technological usefulness of the catalyst—the ease of its separation after the reaction, the possibility of its re-use and regeneration, and sensitivity to poisoning. It is not easy to draw a line between metallic catalysts on carriers and metal complex catalysts linked to polymeric ligands. Complex formation on the surface of a solid (polymeric) carrier takes place when the carrier exhibits a definite complex-forming capacity. Otherwise, for example, as in asymmetric hydrogenation on metals deposited on quartz crystals, one is dealing with deposited catalysts.

Catalysts can be subdivided into the following groups on the basis of the increase of the strength of the bond between the catalytic centre (metal or complex) and the carrier surface.

1. Metal deposited on an inert carrier (for example, nickel on quartz).

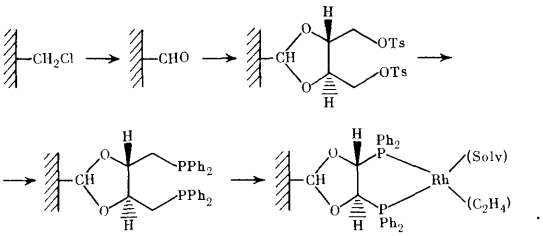
2. Metallic catalyst modified with an optically active organic complex: the complex formed is coordinated to the surface of the catalyst (for example nickel—tartaric acid or nickel—leucine).

3. The complex, which becomes chemically bound to the carrier or metal when a polymeric ligand (a complex forming polymer) is introduced into it (for example, rhodium—polyacrylamide—ethylidenealanine).

A catalyst of the last type is considered below.

Phosphinated polystyrene resins have been used as ligands for metal complex rhodium and platinum hydrosilylation and hydroformylation reactions[75]. The polymeric ligand can be obtained in two ways: (1) by introducing an achiral phosphine into a chiral synthetic or natural polymer; (2) by binding a chiral phosphine to an achiral polymer.

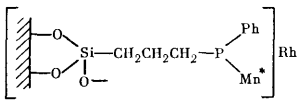
An active chiral metal complex hydrogenation catalyst containing a chiral polymeric ligand was first obtained by Poulin and coworkers[75,76] from Merrifield's resin (polystyrene cross-linked with 2% of divinylbenzene and chloromethylated to an extent of 0.7 mequiv. g^{-1}) bound to DIOP. The chiral polymer was synthesised and the complex [$RhCl(CH_2CH_2)_2$] was immobilised in accordance with the following scheme:



The rhodium complex is formed *in situ*. The hydrogenation was carried out at 20 °C for 12 h in benzene. *R*(−)-2-Phenylbutane with $p = 1.5\%$ was obtained from α-ethylstyrene, while the corresponding soluble complex [Rh.DIOP] gave a product with $p = 15\%$; repeated hydrogenation in the presence of the same catalyst gives a product with $p = 0.6\%$. The relatively inactive *S*(+)-phenyl propionate was also obtained from methyl atropate (the soluble complex gives $p = 7\%$). *N*-Acetamidocinnamic acid, which is insoluble in non-polar solvents, is not hydrogenated at all under the conditions investigated, while in an alcoholic medium the reaction could not be achieved owing to the hydrophobic nature of the polymeric catalyst. Thus the catalyst proved to be relatively unsuitable for hydrogenation, although it exhibited an appreciable enantioselectivity in the asymmetric hydrosilylation of acetophenone by Ph_2SiH_2: the product is *S*(−)-α-phenylethyl alcohol with $p = 29\%$. When the catalyst was re-used, the product with $p = 22\%$ was obtained. For the analogous soluble complex, $p = 28\%$. The use of naphthylphenylsilane as the silylating agent[77] increases the optical yield to 58.5%.

The increase of the ligand/Rh ratio above 2 for the soluble complex results in a loss of enantioselectivity, while that of the polymeric analogue is retained in this instance, an increase of p being observed in other cases. This shows that in the last case the active centres are distributed at fairly long distances from one another and the rigid polymer chain prevents the coordination of the excess diphosphine to rhodium. At the same time it follows from these results that the hydrogenation reaction is much more sensitive to the catalyst structure than hydrosilylation, whereas the enantioselectivities are the same for both the polymeric catalyst and for its soluble analogue.

Immobilised complexes of another type are also active in hydrosilylation. The compound $(EtO)_3Si(CH_2)_2PPhMen$, which reacts with $RhCl_2(CO)$ to form the homogeneous complex (XLVI), has been obtained[77]. Binding of the complex (XLVI) to silica gel yields the complex



(XLVI),

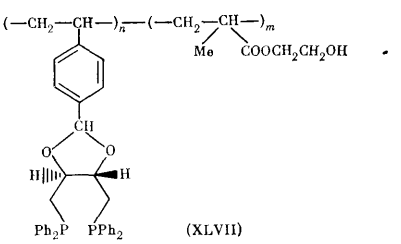
which exhibits enantioselectivity in the hydrosilylation of acetophenone or propiophenone:

$$PhCOR + H_2SiPh_2 \rightarrow PhCH(OSiHPh_2)-R \rightarrow Ph-CH(OH)-R \ .$$

For the optimum ratio Rh/P = 1 : 5, the action of the homogeneous catalyst is comparable to that of the effective [Rh.DIOP] catalyst. It is of interest to note that the alcohol formed has different configurations: S in the former case and R in the latter, although only the S-alcohol is obtained when the complex is re-used or in the presence of an excess of the ligand, apparently as a consequence of the shift of the equilibrium to the left:

$$RhL_n \rightleftarrows RhL_{n-1}Cl + L \ .$$

The employment of a carrier which swells in polar solvents made it possible to obtain an effective hydrogenation catalyst. A cross-linked polymer containing the DIOP residue, swelling in alcohols and other polar solvents, has been synthesised[78]:



(XLVII)

The catalyst was obtained by the interaction of $[RhCl.(C_2H_4)_2]_2$ with compound (XLVII). Acylaminoacrylic acids were hydrogenated at 1–3 atm, which gave a high optical yield of the product (60–86%), comparable to the value of p for the homogeneous complex containing DIOP (63–81%). The antiparallel variation of p and of the overall rate of reaction was noted.

A somewhat different approach was used in a study[79] where $S(-)$-α-phenylethylamine was introduced as the chiral ligand into a rhodium complex containing PPh_3 groups. Two types of polymeric catalysts were obtained. The catalyst based on the IRC-50 ion-exchange resin was prepared by converting the resin into phenylethylammonium salt and by the reaction with $RhCl(PPh_3)_3$. Hydrogenation of N-acetamidocinnamic acid leads to a 50% yield of R-Phe with 17.7% [?(Ed. of Translation)].

Methyl acetoacetate is hydrogenated to $R(-)$-methyl-β-hydroxybutyrate in the presence of a ruthenium complex bound to poly-L-methylethyleneimine (the monomer was obtained from L-alanine).[80,81] The catalyst is obtained *in situ* by adding $RuCl_3$ to a solution of the ligand in an acetate buffer at pH 5.5. The hydrogenation is carried out at 80 to 100 °C and 80 atm. With increase of the ligand/Ru ratio from 2.5 to 10, p increases only slightly (from 0.5 to 5.3%). The antiparallel variation of p and of the overall rate of reaction was noted. The complex $[RuH(PPh_3)poly\text{-}L\text{-}glu]$ is also relatively ineffective in this reaction ($p = 3\%$) and the use of a polymeric ligand—a copolymer of maleic anhydride with S-2-methylbutyl ether—did not lead to the optically active methyl β-hydroxybutyrate[82].

In these examples the manifestation of enantioselectivity by the heterogenised complex is apparently influenced by the chiral structure of the polymeric ligand in the inner sphere of the complex, since it has been shown by the method of the optical rotary dispersion[83] that the polymer does not have a chiral secondary structure. The opposite picture is observed in the case of the complex Cu-poly-L-lysine, in which the helical structure of the polymer plays a decisive role in the manifestation of chiral catalytic properties by the complex[83]. Although this catalyst effects an oxidation and not a hydrogenation reaction, the example is of interest because here the secondary polymer structure has a major influence on the enantioselectivity of the catalyst.

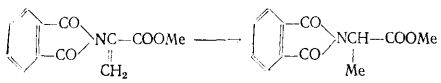
Poly-L-lysine (PLL) has a more rigid helical structure than poly-DL-lysine (PDLL), which has a random uncoiled structure[84,85]. This difference in the secondary structures of the polymers is manifested in the catalytic properties of copper chelates based on them. In the oxidation of D- and L-DOPA (3,4-dihydroxyphenylalanine) in aqueous solution at pH 10.5 in the presence of copper complexes of PLL and PDLL, a difference between the initial rates of oxidation of L- and DL-DOPA in the presence of Cu-PLL was observed. In the helical structure of Cu-PLL four NH_2 groups are coordinated to the copper atom in a plane almost parallel to the axis of the helix, while the amide and OH groups occupy apical positions. The ratio of the rates of oxidation of D- and L-DOPA (v_D/v_L) increases from 1.07 to 1.53 with increase of the fraction of the helical structure of the polymer from 15.6 to 27.6%.[84,85] On the other hand, when the polychelate copper complex of poly-L-α,γ-diaminobutyric acid, which has no helical polymer chain, is used, the specificity of the oxidation vanishes and $v_{DL}/v_L = 1$, which indicates the decisive importance of the helical structure for the manifestation of stereo-selectivity by the polychelate. The distance between the Cu-complexes distributed around the polymer chain is important for the manifestation of the asymmetrising activity. The helical structure of the polymer binds the copper complexes into a three-dimensional structure. The thermodynamic parameters of activation have been determined from the temperature variation of the Michaelis constants, $T\Delta S$ being more negative for L-DOPA than for D-DOPA, indicating a denser transition state with D-DOPA and a correspondingly higher rate of its decomposition.

Metallic hydrogenation catalysts modified by chiral polymers can be assigned to the type of heterogenised metal complex catalysts considered only as a matter of convention.

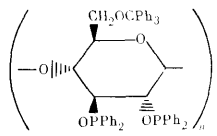
Raney nickel and palladium black have been modified by a chiral copolymer of styrene with D- and L-alanine derivatives of maleimide[86]. The copolymer has three pseudoasymmetric atoms in the chain and in the chiral side group. The question whether the carbon atoms of the polymer chain become chiral was not investigated. Methyl N-acetamidocinnamate was hydrogenated in the presence of nickel and

palladium in solution at atmospheric pressure and 20 °C. The catalysts were modified with 1% solutions of copolymers. *R*(+)-Phe is formed in dioxan, cloroform, and methanol solutions with yields $p = 1.6$ and 1.8%. The change in the acidity of the medium on modification from pH 4 to 9 alters the configuration of the product from *R* to *S*. In acid and neutral media modification apparently results in the formation of imide complexes while in an alkaline medium carboxylate complexes, giving rise to a different stereochemical environment in the complex formed, are produced[86].

Similar studies have been carried out using natural chiral polymers—polysaccharides and proteins. It has been stated that palladium deposited on polysaccharide resins based on dextran and cellulose, can be used in asymmetric hydrogenation[87]. A patent[88] describes the catalyst obtained by treating cellulose with Ph_2PCl and subsequent interaction with $[RhCl(PPh_3)_3]$; the catalyst is active in the reaction

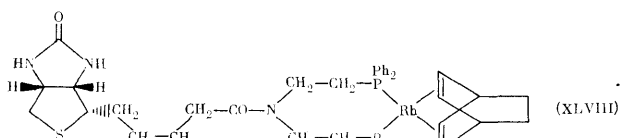


resulting in the formation of the product with $p = 28\%$. The low value of p can be explained[88] by a non-uniform distribution of phosphinite groups in the polymer base. The effect of rhodium catalysts, obtained on the basis of cellulose phosphinite



has been studied in detail[89]. The hydrogenation of α-ethylstyrene to *R*-phenylbutane at 50–120 °C and atmospheric pressure takes place with $p = 57$–77%. An increase of p with increase of the ratio P/Rh to 10 is observed. The antiparallel variation of p and the overall reaction rate has been noted. The re-use of the catalyst leads to a decrease of p to 35%. *N*-Acetamidocinnamic acid is also hydrogenated in the presence of the catalyst with $p = 52\%$ and an overall yield of 17.5% (reaction conditions: P/Rh = 11.5, 50 °C, benzene–ethanol solvent, reaction time 7 days).

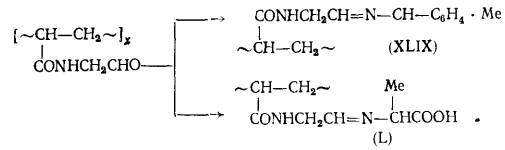
The binding of $Rh(PPh_3)_2$ to proteins leads to the formation of a chiral catalyst for the hydrogenation of *N*-acetamidoacrylic acid[90]. In this case the chiral tertiary structure of the protein (avidin, lysozyme, albumin) creates the necessary chiral environment for the metal complex. The study has been carried out mainly on avidin, whose molecule consists of four identical subunits linked to biotin. The complex is synthesised as follows: biotin is converted into a diphosphine derivative, which gives rise to the complex(XLVIII) *in situ*:



(XLVIII)

The protein and the complex (XLVIII) are added to a solution of the substrate and the reaction is carried out at 1.5 atm and 0 °C for 48 h. Optically active *N*-acylalanine is formed. The complex (XLVIII) is itself a chiral catalyst and the introduction of the protein has little effect on the overall reaction rate. However, whereas in the absence of the protein $p < 2\%$, when one equivalent of avidin is introduced the optical yield rises to 44%. Lysozyme and albumin proved to be relatively ineffective: $p \leq 2$–5%. Preliminary treatment of avidin with biotin reduced sharply the enantioselectivity of the catalyst and p falls to 4%. Hence it follows that the active centre constitutes a formation in which the complex (XLVIII) is linked to the protein via the biotin in the protein molecule.

The catalyst based on a polymer containing aldehyde groups exhibited a high enantioselectivity. The aldehyde groups in the polymer were bound to PEA or alanine with formation of a polymer swelling in organic solvents:



(XLIX)

(L)

On treatment of compound (XLIX) or (L) with $[Rh(COD).Cl]_2$, enantioselective heterogenised metal complex catalysts are formed and the catalyst based on compound (XLIX) does not differ in its enantioselectivity from low-molecular-weight catalysts containing chiral PEA or Schiff bases, while the catalyst based on compound (L) as well as the complex [Rh.benzylidenealanine] exhibited a very high enantioselectivity: the hydrogenation of methyl-*N*-acetamidocinnamate (50 °C, atmospheric pressure, methanol solvent) results in the formation of *S*-phenylalanine with $p = 94.9$–97.6%.[91]

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Thus an extensive search has been carried out for effective metal complex catalysts based on chiral ligands, mainly phosphines, starting with readily available sources of optically active compounds (tartaric acid, phenylethylamine, menthol, hydroxyproline, and monosaccharides). Highly effective catalysts have been obtained, but these exhibit a high enantioselectivity only for a limited number of substrates and the spectrum of their activity is difficult to guess beforehand. The catalytic systems created on the basis of readily available optically active compounds can be used for the preparative synthesis of certain valuable chiral compounds (for example DOPA in an optically pure state). However, the unsuitability for technological applications of soluble metal complex catalysts limits their applicability and makes it necessary to seek systems incorporating a polymeric ligand, i.e. the catalytically active complex must be bound to a polymer chain or a carrier in order to convert the homogeneous catalyst into an insoluble "heterogenised" catalyst. The present review has shown that promising data have been obtained on these lines.

Despite the advances made in enantioselective hydrogenation, the deficiencies of these investigations should be noted: the studies have been performed with a purely experimental selection of systems and detailed investigations of the reaction mechanism in order to discover the relation between the enantioselectivity and reactivity of the complexes and the relation between the structure of the ligand and the complex, on the one hand, and the structure of the substrate molecule, on the other, have not been made. So far no attempts have been made to find general rules governing the action of chiral metal complex catalysts in a specific reaction, relating, for example, the thermodynamic stability of the complex to its overall activity and enantioselectivity. The discovery of such rules, for example, in asymmetric hydrogenation on metallic catalysts modified with chiral aminoacids, proved to be extremely useful in predicting their enantioselective activity[7].

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The Chemistry of Perfumes Based on Labdane Diterpenoids

P.F.Vlad

The advances in the synthesis of C_{14}–C_{19} perfumes derived from bicyclic labdane diterpenoids and their enantiomers as well as data concerning the sources of the starting materials are presented. The dependence of the odour of the above compounds on their structure and stereochemistry and the questions arising in the manufacture of some of them and their practical applications are considered.
The bibliography includes 242 references

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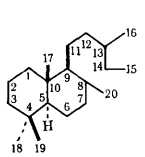
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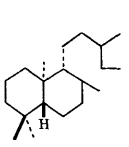
I. INTRODUCTION

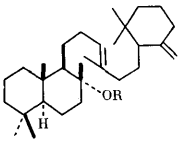
Derivatives of labdane (I) [1–4] occupy an important place among diterpenoids. They are stable biosynthetic intermediates in the conversion of aliphatic compounds into cyclic compounds, including kauranoids, which are precursors of gibberellins[5]. Derivatives of both labdane and *enantio*-labdane (II) (eneruane) are widely distributed in nature[3]. In certain plants they are present in large amounts, can be readily isolated, and have therefore been known for a long time. Labdanoids have frequently been used as the starting materials in syntheses (including biomimetic syntheses) of tricyclic and tetracyclic diterpenoids[6]. All these factors led to the accumulation of extensive factual data on the chemistry of these compounds.

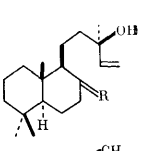
An important stimulus for the development of the chemistry of labdanoids proved to be the discovery among their transformation products of substances with an intense smell of ambergris[7,8]—full substitutes of ambergris, which is a product of the metabolism of sperm whales and is one of the most valuable types of raw material for perfumery[9]. Its odour is due to the products of the autoxidation of the main component—ambrein (3) (a triterpene)[10,11]. Simultaneously with the elucidation of the chemical nature of the perfume components of ambergris, it was noted[7] that the products of the oxidation of the labdanum glycol sclareol (4), isolated from the muscat sage, also have the odour of ambergris. These observations gave rise to a series of studies on the resolution of sclareol[8,12,13], which culminated in the preparation of a series of interesting compounds with the ambergris odour.

Subsequently such substances were obtained also from other labdanoids. The majority of these contain 16–18 carbond atoms and have effective fixative properties.


(1)


(2)


(3) R=H
(137) R = THP


(4) R = $\swarrow^{CH_3}_{OH}$
(5) R = CH_2

The industrial manufacture of perfumes based on readily available labdane diterpenoids was begun in the 1950's[14–20]. These include sclareol, isolated from the waste products of the essential oil industry[21–29], and manool (V), isolated from the wood of the yellow pine[30,31]. The main raw materials for the manufacture of sclareol are in the USSR. Our perfume industry manufactures on its basis two products with the odour of ambergris—ambrial[19,32–34] and ambroxide[20,32].

During the last 10–15 years, there has been a considerable growth of interest in the perfumes obtained from labdanoids, as shown by the numerous publications. The reason for this is the continually growing demand for these substances throughout the world and the continuously decreasing number of sperm whales.

Another cause of the intensification of this research is the study of the dependence of odour on the structure of substances, a problem which is far from being solved[35]. The rigid *trans*-decalin skeleton, the possibility of obtaining enantiomeric compounds, as well as the extensive factual data which have accumulated make perfumes based on labdane diterpenoids a convenient model for tracing the dependence of odour on structure.

The intensification of studies on labdanoids was also promoted by the fact that large amounts of these substances as well as their cleavage products are present in tobacco[36–44], imparting to it valuable organoleptic properties. The addition of these compounds to various kinds of tobacco improves its quality[45–48].

The majority of the perfumes considered have been obtained from labdanoids. Several oxides of the *enantio*-labdane series, which also proved to have the odour of ambergris, have been synthesised quite recently[49,50].

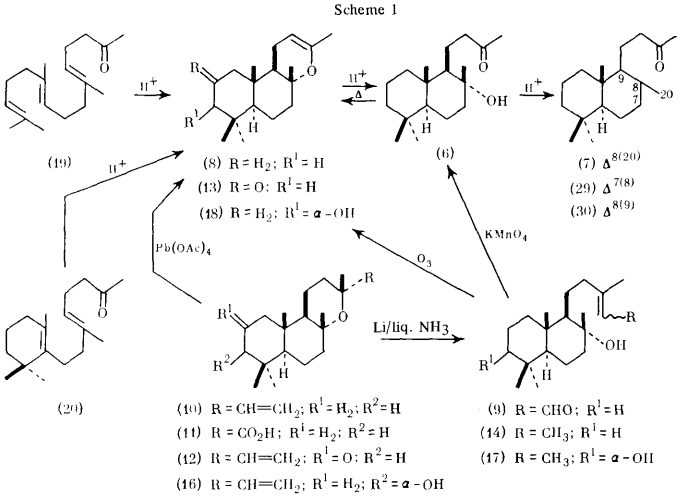
The present review surveys data on the chemistry of perfumes obtained from labdane diterpenoids and published up to 1981. Certain reviews[51–53] and monographs[3,54] devoted to other problems include isolated information concerning the topic under consideration, but there have been no systematic surveys. We have used the system of numbering of carbon atoms in labdane proposed by Kocker and Halsall[1].

II. 14,15-BISNOR-13-LABDANONES—IMPORTANT INTERMEDIATES IN THE SYNTHESIS OF PERFUMES

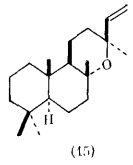
When labdanoids are cleaved to C_{15}–C_{18} compounds, derivatives of 14,15-bisnor-13-labdanone are always formed. 8α-Hydroxy-14,15-bisnor-13-labdanone (6) and 14,15-bisnorlabd-8(20)-en-13-one (7) are of greatest interest for the synthesis of perfumes. The hydroxyketone (6) was

obtained on oxidising sclareol[55–57]. It is unstable and is converted into the oxide (8) on standing or heating (Scheme 1).

Scheme 1



The melting point indicated for this compound therefore varies from 90° to 122 °C.[55,58–60] The reverse reaction, involving the opening of the oxide (8), takes place on treatment with acids or semicarbazide[56,58]. By altering the conditions, the sclareol oxidation reaction can be directed preferentially towards the formation of substances (6) or (8), which have been obtained also on oxidation of certain sclareol transformation products, for example the aldehyde (9):[58,60]

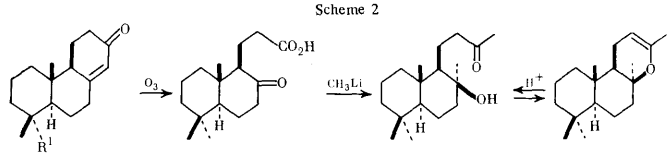

(15)

The enol ester (8) has also been synthesied from manoyl oxide (10) as a result of its oxidation with the acid (11) [61] and the decarboxylation of the latter[62]. The keto-oxide (13) has been obtained similarly from 2-oxomanoyl oxide (12) [63] (see Scheme 1). 2-Oxomanoyl oxide can also be reduced quantitatively to manoyl oxide without isolating it from the pine resin[63]. On a preparative scale, a different method of converting the oxide (10) into the hydroxyketone (6) is more convenient: the hydrogenolysis of the oxide to dihydroabienol (14) [64] and its oxidation [the yield of the hydroxyketone (6) was 94%]. The hydroxyketone (6) can be obtained in this way also from 13-epimanoyl oxide (15). The hydrogenolysis of 3α-hydroxymanoyl oxide (16) leads to the product (17), whose ozonisation gives rise to the alcohol oxide (18).[65]

The enol ester (8) has also been synthesised by cyclising *trans, trans*-farnesylacetone (19) [66] or *trans*-β-monocyclofarnesylacetone (20) [67] (see Scheme 1). Its stereoisomers have been obtained analogously[68]. However, the method is complex, since the starting materials are difficult to obtain.

The epimer (21) of the hydroxyketone (6) at the C(8) atom is formed together with the enol ester (22) [58] when methyl-lithium reacts with the ketoacid (23)—the product of the ozonisation of podocarp-8(14)-en-13-one (24). The unsaturated ketone (24) was synthesised from manool[30,69] and neoabietic acid (25) [70] or *m*-methoxyphenylacetylene[58] (see Scheme 2).

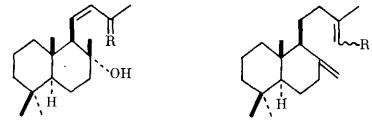
Scheme 2



The enol ester (8), the hydroxyketone (6), and its dehydro-derivative (26) have been detected in tobacco[39]. Compound (26) was first isolated from the resin of the Siberian larch[71]. It is the product of the autoxidation of neoabienols (27) and (28).[72–75] Its hydrogenation gives rise to the hydroxyketone (6).[71]

14,15-Bisnorlabd-8(20)-en-13-one is a product of the dehydration of the hydroxyketone (6). However, the dehydration of the latter leads to 14,15-bisnorlabd-7-en-13-one (29) [56,58,76] or to a mixture of the isomeric compounds (7), (29), and (30),[77] which has also been obtained in the oxidation of sclareol[78,79]. On dehydration of the stereoisomeric hydroxyketone (21), a mixture of the ketones (29) and (30) is obtained[70].

14,15-Bisnorlabd-8(20)-en-13-one was first obtained in the oxidation of manool with potassium permanganate[30]. The structure was demonstrated by Schenk et al.[80], who modified the method of oxidation described in another communication[81] (see also Ohloff[82] and Demole and Weust[83]).

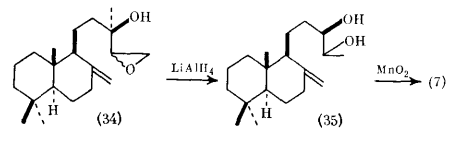

(26) R = O
(27) R = CHCH3; Δ13-*cis*
(28) R = CHCH3; Δ13-*trans*
(31) R = CH2Br
(32) R = CHO
(33) R = CH2OAc

The yield of the ketone (7) is 36–40% and does not increase when the oxidation conditions are varied[84–86]. It is also formed in a low yield of (14%) in the ozonisation of manool[84].

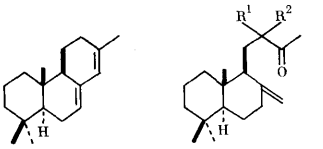
Two- and three-stage methods of synthesising the ketone (7) from manool are known. Thus on treatment with certain oxidants[85,87] or via the bromide (31),[88] manool is converted into a mixture of the *cis*- and *trans*-aldehydes (32), which are oxidised to the ketone (7).[85] The acetate (33), which is a product of the substitution of the bromide (31), also gives rise to the ketone (7) on oxidation[88]. Compound (31), in a mixture with its isomers and dibromides, is also formed on bromination of sclareol[88–91], which permits the synthesis of the ketone (7) from sclareol. On the other hand, it is known[82] that sclareol diacetate yields manool acetate on pyrolysis. This reaction can be achieved more simply by heating sclareol with acetic anhydride and calcium carbide[92] or pyridine[93]. In the latter case the product consists of a complex mixture of substances.

An interesting conversion of manool into the ketone (7) in 90–95% yields, involving its selective epoxidation to a mixture of epoxides (34), the reduction of the latter to a mixture of diols (35), and the cleavage of the latter by various oxidants, the best of which is manganese dioxide, has been described (see Scheme 3)[94]. This series of transformations can be achieved without isolating the intermediates.

Scheme 3



14,15-Bisnorlabd-8(20)-en-13-one has been detected in tobacco[42] and in certain types of resin[95,96]. In one of them[95] it is present together with its Δ^{11}-dehydro-derivative, formed on dehydration of the hydroxyketone (26).[71] We may note that the ketone (7) is unstable: it undergoes autoxidation on standing[79] and cyclises to the hydrocarbon (36) under the influence of acids[13,97,98].

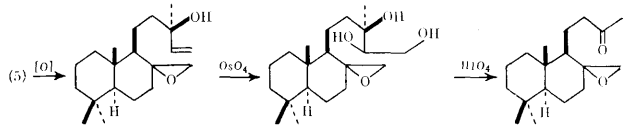


(36) (44) $R^1 + R^2 = CH_2$

(45) $R^1 = CH_2OCH_3$; $R^2 = H$

8,20-α-Epoxy-14,15-bisnor-13-labdanone (37), detected in *Dacrydium kirkii*, is of great importance for the synthesis of perfumes[99]. It was obtained from the manool monoepoxide (38), which is formed together with its steroisomer (39) when manool is oxidised by peracids (see Scheme 4). The ratio of the stereoisomers (38) and (39) varies within wide limits as a function of the reactants and the reaction conditions[91, 99-101]. On interaction with osmic acid, the epoxide (38) gives the epoxytriol (40), which is cleaved by periodic acid to the epoxyketone (37).[100,102] This transformation can be achieved in a single stage, using catalytic amounts of osmic acid[100,102,103]. The same result is obtained when the unsaturated epoxide (38) is ozonised[104].

Scheme 4



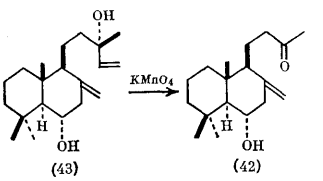
(38) α-epoxy (40) (37) α-epoxy

(39) β-epoxy (41) β-epoxy

Compound (37) and a small amount of its stereoisomer (41) are formed when the ketone (7) is oxidised with *m*-chloroperbenzoic acid[85,100,104]. Monoperphthalic acid leads mainly to its further transformation products[85]. The expoxyketones (37) and (41) have been detected among the sclareol oxidation products[79].

6-α-Hydroxy-14,15-bisnorlabd-8(20)-en-13-one (42)—the product of the oxidation of larixol (43) [105-109] which is one of the main components of the resins of different species of larch[110-115]—is of great interest for the synthesis of perfumes.

The forms of the ketone (7) oxidised in the C(19)-position have been detected in natural sources[116,117].

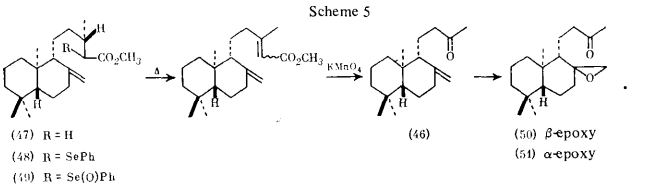


(43) (42)

When the ketone (7) is condensed with formaldehyde, it gives rise to a mixture of C_{19} products (44) and (45), which have also been used to synthesise perfumes[118].

The synthesis of the optical isomer (46) to the ketone (7) via Scheme 5 from the ester of eperuic acid (47) [119] has been achieved recently[49]. The selenium derivatives (48) and (49) are of key importance in this synthesis. Thus the possibility, in principle, of using labdanoids and their optical isomers with a saturated side chain in the syntheses of perfumes has been demonstrated, which makes it possible to extend significantly the range of starting materials for such syntheses.

Scheme 5



(47) R = H (46) (50) β-epoxy

(48) R = SePh (51) α-epoxy

(49) R = Se(O)Ph

When the ketone (46) is epoxidised with *m*-chloroperbenzoic acid, it gives rise to a mixture of the epoxides (50) and (51), in which the former predominates.

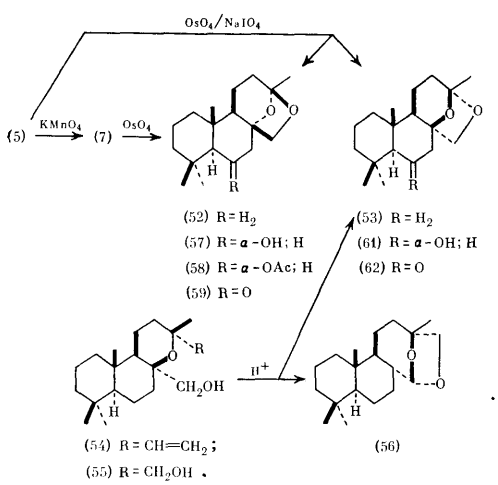
III. THE SYNTHESIS OF PERFUMES FROM LABDANE DITERPENOIDS

1. C_{18} and C_{19} Perfumes

The group of C_{18} perfumes consists mainly of intramolecular ketals. The first of these [compound (52)], which has an intense odour of ambergris, was discovered among the products of the oxidation of manool with permanganate[81] (see Scheme 6). Its structure was confirmed by the fact that it is formed on interaction of the ketone (7) with osmic acids[8,103] and also by NMR and data for its hydrogenolysis[100]. Compound (52) has also been obtained on oxidation of manool with osmic acid and sodium periodate[100] or, together with its diastereoisomer (53), on isomerisation of the epoxyketone (37),[100,102-104] which occurs in the course of its formation on oxidation of the ketone (7) with monoperphthalic acid[86]. It was thought that the ketal (53) also has a powerful odour of ambergris, but, according to the latest data[50], it lacks such an odour.

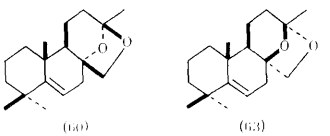
The main method of opening the epoxide ring in compound (37) involves nucleophilic attack by the carbonyl oxygen on the C(8) atom with inversion of configuration, since, for a ratio of the epoxyketones (37) and (41) in the initial mixture of 16:1, the content of the ketal (53) in the reaction products changes from 50% [118] to 70%,[100,102-104] depending on the conditions. Partial opening of the epoxide ring occurs also via the S_N1 mechanism, since, in the presence of 6% of the epoxyketone (41) in the initial mixture, the yield of the ketal (52) reaches 25% and, in the isomerisation of the pure epoxyketone (37) under the same conditions, the yield is 10%.[83] If the isomerisation of the mixture of the epoxyketones (37) and (41) is carried out with silicic acid in a heterogeneous medium, then the opening of the opoxide ring in compound (37) takes place preferentially via the S_N1 mechanism and the ketal (52) predominates in the reaction products[83].

Scheme 6



A theoretically interesting method of converting manool into the ketal (53) has been described[120]. Manool monoepoxide is isomerised with an acid to the alcohol oxide (54). Successive ozonisation, reduction, and hydrolysis of its acetate lead to the diol (55), which is converted by acids into a mixture of the ketals (53) and (56) (see Scheme 6).

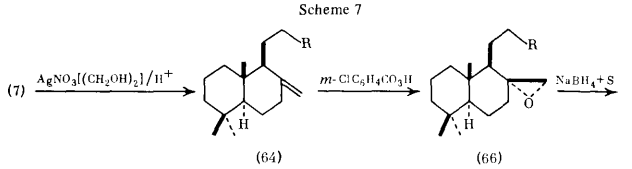
In order to expand the raw material resources for the preparation of the ketals (52) and (53) and their analogues, methods have been developed for their synthesis from other labdanoids. Thus the oxidation of larixol[108] and its acetate[106–110] results in the formation of the hydroxyketal (57) and its acetate (58) respectively. The product of the oxidation of the former—the ketoketal (59)—undergoes the Wolff-Kishner reduction to the ketal (52),[109] which has also been obtained from compound (57) on dehydration of the latter to compound (60) and its subsequent hydrogenation[108, 121]. Only the ketal (60) has an odour. An analogous synthesis of the ketals (53) and (61)–(63) from the hydroxyketone (42) has been described in a patent[121]; one of the products [compound (63)] is a perfume[118]:

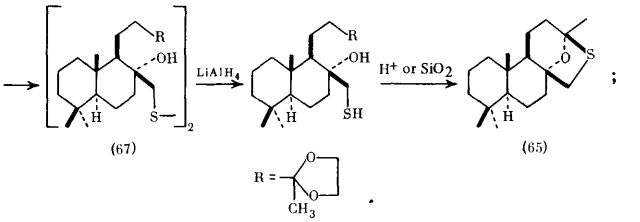


Compounds (52) and (53) have been discovered also among the products of the oxidation of sclareol[122,123].

The thio-analogue (65) of the ketal (52) has been synthesised from the ketal (64) of the ketone (7).[97] The conversion of the ketone (7) into the ketal by treatment with silver nitrate and the formation of the sulphur-containing dimer (67) when the epoxide (66) interacts with the sulphur-treated sodium tetrahydroborate are key stages in the synthesis. The thioketal (65) has a weak woody odour.

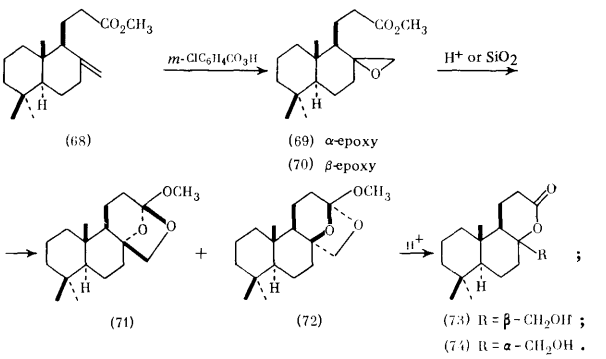
Scheme 7



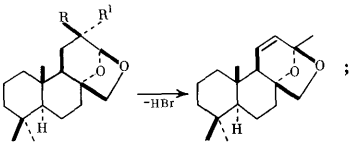


Interesting perfume analogues of the ketals (52) and (53) have been described[83]. The ester (68), which is the product of the oxidation of the ketone (7),[81,85] is oxidised by *m*-chloroperbenzoic acid to an 8 : 1 mixture of the epoxyesters (69) and (70) (Scheme 8), which isomerise on treatment with acid to a mixture of the orthoesters (71) and (72), in which the latter predominates. This conversion of the ester (68) can be achieved in a single stage when the epoxidation is carried out at a higher temperature. When the epoxyester (69) is isomerised with silicic acid, the orthoester (71) predominates in the reaction product, i.e. there is a complete similarity in the behaviour of compounds (37) and (69). The structure and stereochemistry of the orthoesters (71) and (72) have been confirmed by spectroscopic methods and by the formation, following their acid hydrolysis, of the known 20-hydroxyambreinolide (73) and its epimer (74).

Scheme 8

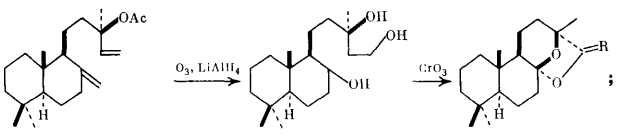


The reaction of the ketal (52) with bromine converts it into a mixture of compounds (75)–(77).[124] The monobromo-derivative (75) is resistant to the action of alkalies, while its isomer (76) splits off hydrogen bromide, albeit with difficulty, and is converted into the scented ketal (78):



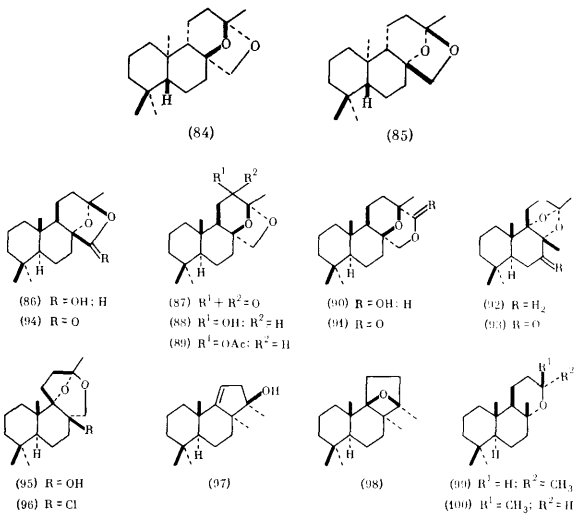
When manool acetate (79) was ozonised, the triol (80), which can be oxidised to the perfume (81), was isolated in a low yield (see Scheme 9)[125]. The ozonisation of manool itself leads to the formation (together with other products) of the hemiacetalketal (82), which has no odour. However its oxidation product, the lactone (83),[126] which can be obtained from manool in a single stage[85], is a perfume.

Scheme 9



(79) (80) (81) R = H_2; (82) R = OH; H; (83) R = O.

The enantiomers (84) and (85) of the ketals (52) and (53), the first substances of the *enantio*-labdane series which also possess the odour of ambergris[50], have been obtained recently[49] by the isomerisation of the epoxyketones (50) and (51):



(84) (85)

(86) R = OH; H (94) R = O

(87) $R^1 + R^2$ = O (88) R^1 = OH; R^2 = H (89) R^1 = OAc; R^2 = H

(90) R = OH; H (91) R = O

(92) R = H_2 (93) R = O

(95) R = OH (96) R = Cl

(97)

(98)

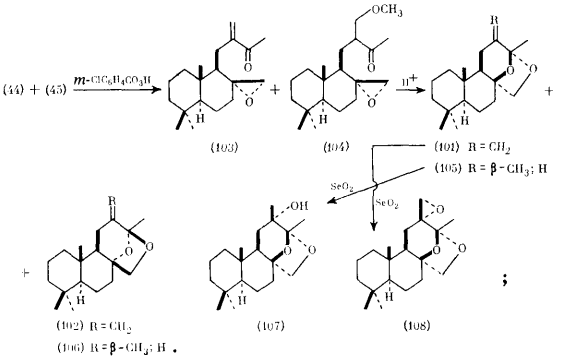
(99) R^1 = H; R^2 = CH_3 (100) R^1 = CH_3; R^2 = H

In the course of the search for perfumes, the intramolecular ketals (86),[124] (87)–(91),[100] (92) [125] (this substance has also been found in tobacco[43]), (93),[80] (94),[85] and (95) and (96) [127] were synthesised, but none of them are scented.

When the ketone (7) is irradiated with ultraviolet light, a mixture of 12 substances is formed, two of which, compounds (97) and (98), have the odour of ambergris[128]. When the enol ester (8) is hydrogenated, a mixture of oxides (99) and (100), which have also been detected in tobacco[43], is produced. The oxide (100) has the odour of ambergris[129].

Few C_{19} perfumes are known. The reason for this is apparently their low volatility owing to their high molecular weights. The scented substances (101) and (102) have been obtained by treating the epoxides (103) and (104), which are the products of the oxidation of the ketones (44) and (45),[118] with acid (see Scheme 10). Simultaneously with isomerisation, the epoxyketone (104) splits off methanol. The products (105) and (106) of the hydrogenation of the ketals (101) and (102) and the products (107) and (108) of the oxidation of the ketals (101) and (105) with selenium dioxide are also scented.

Scheme 10



(102) R = CH_2 (106) R = β-CH_3; H. (103) (104) (101) R = CH_2 (105) R = β-CH_3; H (107) (108)

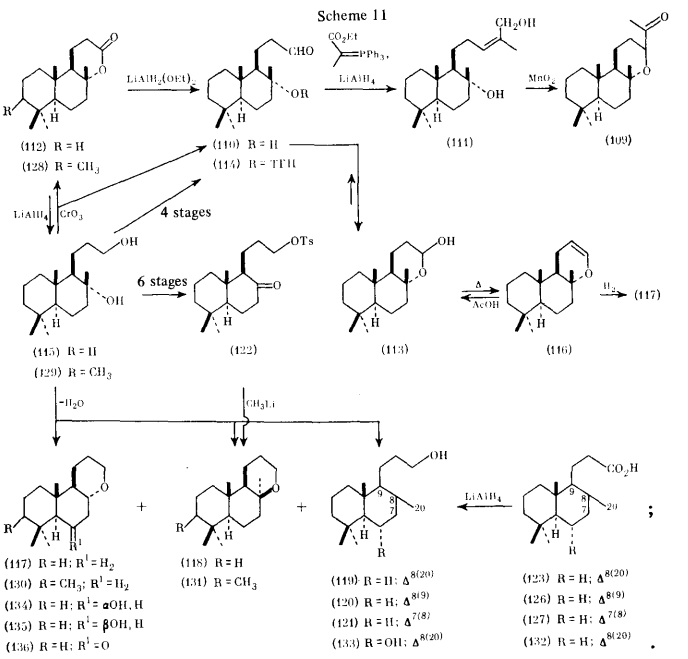
Yet another C_{19} perfume [compound (109)] has been synthesised in accordance with Scheme 11 below from ambreinolal (110). The oxidation of the diol (111) with activated manganese dioxide takes place in an unusual manner with the cleavage of the C–C bond and the formation of a tetrahydropyran ring[130].

2. C_{17} Perfumes

This group of substances includes the perfume components of ambergris. Depending on the conditions, the oxidative cleavage of ambrein leads to the formation of ambreinolal[131–133] or ambreinolide (112).[10,11,131,134] Under natural conditions, this is caused by light and atmospheric oxygen and is catalysed by copper ions[9] and photosensitisers[135]. Ambreinolal exists in the form of the cyclic hemiacetal (113) [131] and its derivatives, for example, the tetrahydropyranyl derivative (114), can be obtained only indirectly from ambrein[136] or ambreinolal (115)—the product of the reduction of ambreinolide[8,131,137].

On vacuum distillation, compounds (113) and (114) are converted into the oxide (116) [131–133,136–141]—the first known derivative of *trans*-decalin with the odour of ambergris, which enters into the composition of the volatile component of ambergris. The reverse hydration of the oxide (116) to the hemiacetal (113) is also possible (Scheme 11).

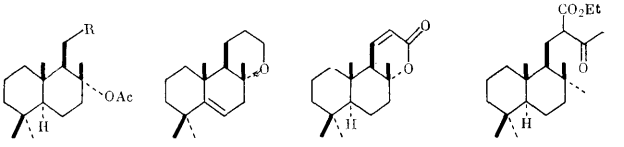
Scheme 11



(112) R = H (128) R = CH_3 (110) R = H (114) R = THH (111) (109) (115) R = H (129) R = CH_3 (122) (113) (116) (117) (117) R = H; R^1 = H_2 (130) R = CH_3; R^1 = H_2 (134) R = H; R^1 = αOH, H (135) R = H; R^1 = βOH, H (136) R = H; R^1 = O (118) R = H (131) R = CH_3 (119) R = H; $\Delta^{8(20)}$ (120) R = H; $\Delta^{8(9)}$ (121) R = H; $\Delta^{7(8)}$ (133) R = OH; $\Delta^{8(20)}$ (123) R = H; $\Delta^{8(20)}$ (126) R = H; $\Delta^{8(9)}$ (127) R = H; $\Delta^{7(8)}$ (132) R = H; $\Delta^{8(20)}$.

The hydroxyaldehyde (110) has been obtained in a low yield (~20%) by the reduction of ambreinolide by complex hydrides[130,142] and by the oxidation of the diol (115) by chromium trioxide[136] (see Scheme 11). According to Demole and Wuest[83], ambreinolide is formed in the latter case.

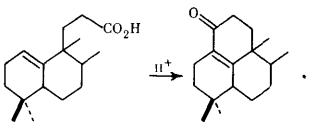
When the oxide (116) is hydrogenated, the dihydro-derivative (117), with a strong odour of ambergris, is formed[133]; it has also been synthesised by the dehydration of ambreinolol (115) by various reagents[8,15,131,137,143]. The stereochemistry of compound (117) follows from the fact that its oxidation yields ambreinolide[137]. Apart from the oxide (117), the dehydration of the diol (115) leads to the formation of the oxide (118) and a mixture of scented alcohols (119)–(121). The stereoselective synthesis of the oxide (118) from the diol (115), in which the key stage is the interaction of the ketotosylate (122) with methyl-lithium, has been achieved recently[50] (see Scheme 11). In contrast to its epimer (117), the product has no odour. The alcohol (119) has also been obtained from the acid (123), synthesised from ambreinolide[144] and the hydroxyacetate (124)—the product of the ozonolysis of the oxide (8),[7] or by the reduction of the acetoxyaldehyde (125), which is also formed when the oxide (8) is ozonised[144]. The last synthesis of the acid (123) constitutes one of the possible ways of converting labdane diterpenoids into C_{17} compounds, a characteristic of which is cleavage to C_{16} compounds. Finally the acid (123) has been synthesised by the hypohalite oxidation of the ketone (7).[80,81] Ambreinolide has also been converted into the isomeric acid (126)[10,145] and into the mixture of the acids (123), (126), and (127)[85,137] and their esters[10], which can be reduced to a mixture of the alcohols (119)–(121). The acid (126) has been detected among the products of the cleavage of the diterpenoid marrubiin[146]. Its most convenient synthesis is the hypohalite oxidation of the ketone (30).[58,77,85] The full multistage synthesis of the racemic acid (126) has been achieved using *m*-methoxyphenylacetylene as the starting material[58]. The synthesis can be greatly simplified by taking into account the fact that the intermediate (8-epi-ambreinolide) can be converted into a mixture of esters of the acids (123), (126), and (127), like ambreinolide, and can be synthesised from podocarp-8-(14)-en-13-one in only two stages[58].



(124) R = CH_2OH
(125) R = CHO
(137) (140) (141)

Scented analogues of the oxides (117) and (118) are known. Thus the product of the reduction of 3-methylambreinolide (128), namely the diol (129), gives rise on dehydration to a mixture of the oxides (130) and (131), which have a fruity smell[147], while the product of the oxidation of the hydroxy-ketone (42), i.e. the hydroxyacid (132), has been reduced to the diol (133), which cyclises with simultaneous epimerisation at C(6) to a mixture of the oxides (134) and (135).[120,148] Like the keto-oxides (136), they are not scented[62], but the oxide (137) obtained on their dehydration has the odour of ambergris[121,148].

On treatment with sulphuric acid, ambreinolide rearranges to the acid (138), which subsequently cyclises to the carbonyl compound (139), with a phenalan structure which has a strong odour of ambergris[137,149]:

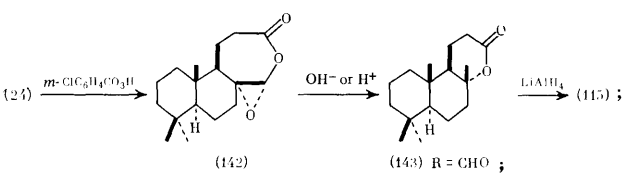


(138) (139)

The above data show that ambreinolide is an important substance for the synthesis of valuable perfumes. Ambreinolide and Δ^{12}-dehydroambreinolide (140) are present in small amounts in tobacco[39], but there are no natural sources with a high content of these substances. The problem therefore arose of the synthesis of ambreinolide. In one of its first syntheses it was obtained from the hydroxyketone (6) (yield 68%)[59,150]. On interaction with diethyl carbonate, it gives rise to the hydroxyketoester (141), the ketone cleavage of which leads to ambreinolide. The latter has also been obtained by the cyclisation of the acid (123)[80] or by the reduction of the product of the epoxidation of its ester (69) to the diol (115) and subsequent oxidation of the latter with chromium trioxide[83]. The isomeric acid (126) also cyclises to ambreinolide[58,85]. In the method of its synthesis described by Bigley et al.[58], the intermediate is podocarp-8-(14)-en-13-one, which was converted into ambreinolol in accordance with Scheme 12.[151]

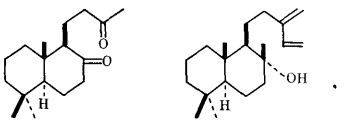
Another pathway leading to the tosylate (144) was mentioned earlier by Demole and Wuest[83].

Scheme 12



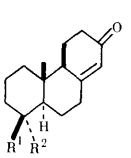
(142)
(143) R = CHO;
(73) R = CH_2OH;
(144) R = CH_2OTs.

The ketone (24) is an important intermediate in the synthesis of many compounds. It is formed on cyclisation of the diketone (145), produced as a result of the oxidation of manool by various oxidants[30,70,80,84,85,151,152]:

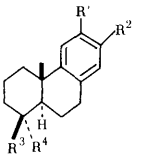


(145) (151)

Podocarpenone (24) and its derivatives with functional groups at the C(18) and C(19) carbon atoms can be obtained relatively simply from readily available substances such as resin acids. Thus neoabietic acid has been converted into the ketoester (146),[153] 13-desisopropyl-13-methoxydehydroabietate (147) has been converted into the hydroxyketone (148),[154] and podocarpic acid (149) has been converted into the hydroxyketone (150).[155] The ketoester (146) has been converted into podocarpenone[70].



(146) $R^1 = CH_3$; $R^2 = CO_2CH_3$
(148) $R^1 = CH_3$; $R^2 = CH_2OH$
(150) $R^1 = CH_2OH$; $R^2 = CH_3$

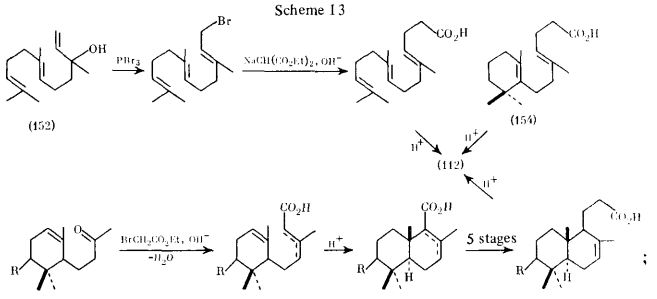


(147) $R^1 = H$; $R^2 = OH$; $R^3 = CH_3$; $R^4 = CO_2CH_3$
(149) $R^1 = OH$; $R^2 = H$; $R^3 = CO_2H$; $R^4 = CH_3$

A convenient method of synthesis of ambreinolide consists in the oxidation of isoabienol (151),[156] which has been synthesised from sclareol[156] and enters into the composition of the resin of the Siberian fir[157,158] and the evergreen cypress[75]. However, isoabienol is difficult to obtain. The situation changed after it was observed[159] that it is contained in a large amount in the needles of the common pine.

Several syntheses of racemic ambreinolide have been developed. They all consist of many stages and the starting materials are difficult to obtain. Scheme 13 shows that nerolidol (152),[160] dihydro-α-ionone (153),[161] or β-monocyclofarnesylacetic acid (154) [162] have been used as the starting materials. 3-Methylambreinolide has been obtained analogously from methyldihydro-α-ionone (155).[147]

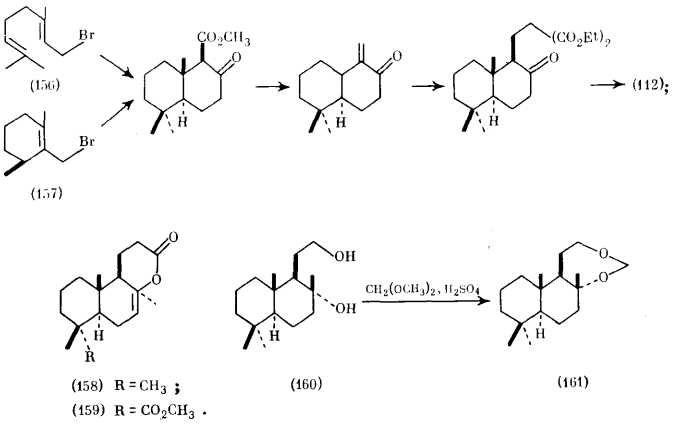
Scheme 13



(153) R = H;
(155) R = CH_3.

A novel synthesis of ambreinolide from geranyl bromide (156) and β-cyclogeranyl bromide (157), the principal stages of which are presented in Scheme 14, has been described[163]. On the whole, very numerous syntheses of ambreinolide have been described, but none is suitable for industrial application.

Scheme 14

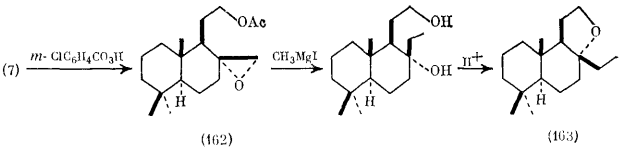


(158) R = CH_3;
(159) R = CO_2CH_3.

The enol lactone (158), obtained from the ketoacid (23), is used as an odorant for tobacco. The ketoacid (23) is formed together with other substances when the pyrolysis products of ambreinolide or the dehydration products of sclareol are ozonised[48]. The lactone (159) has been synthesised for the same purpose[164].

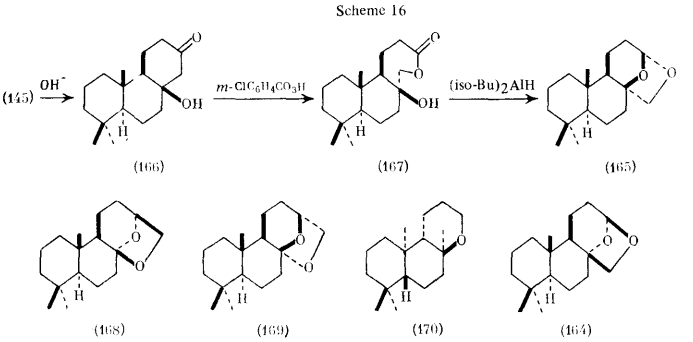
The interaction of the glycol (160), which is a product of the transformation of sclareol[8], with dimethoxymethane gives a low yield of the acetal (161) with a strong odour of ambergris[125]. The scented C_{17} oxide (163) has been obtained from the ketone (7), as shown in Scheme 15.[165].

Scheme 15



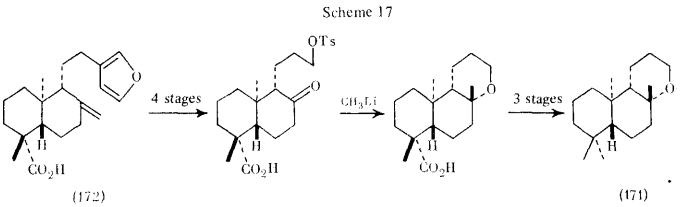
When 20-hydroxyambreinolide is reduced with di-isobutylaluminium hydride, the scented ketal (164) is formed. Its diastereoisomer (165) has been obtained analogously from the hydroxylactone (167)—the product of the oxidation of 8-β-hydroxy-13-podocarpanone (166) (see Scheme 16)[151]. The isomers (168) and (169) of these ketals, which have been synthesised from podocarpenone (24),[166] are not scented.

Scheme 16



As in the case of compounds of the labdanum series, the oxide (170) of the *enantio*-labdane series has been recently obtained from the ketone (46).[50] Its epimer (171) has been synthesised stereoselectively from daniellic acid (172) in accordance with Scheme 17:

Scheme 17



The oxides (179) and (171) have the odour of ambergris.

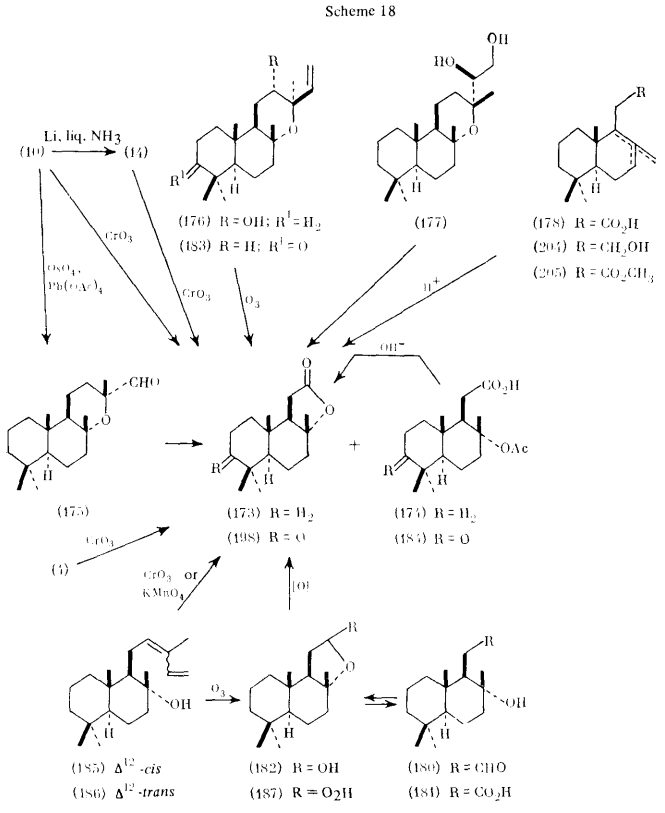
3. C_{16} Perfumes

This group includes a whole series of substances which can serve as full substitutes of ambergris and can be obtained fairly simply from many readily available labdanoids.

One of the main starting materials for these syntheses has been the γ-lactone norambreinolide (173), obtained in a small amount among the ambrein oxidation products[167] and found in tobacco[39]. Together with the acetoxyacid (174), it

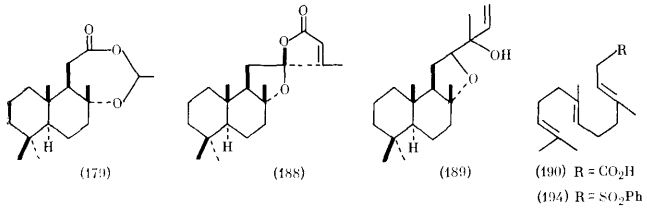
was obtained for the first time by the oxidation of sclareol[23, 55,168,169]. The acetoxyacid (174) gives rise to the lactone (173) on hydrolysis[125] (Scheme 18). According to a patent[170], when the oxidation product is hydrolysed and converted into a lactone, the yield of the lactone reaches 65%, but this method is fairly cumbersome. The method involving the oxidation of sclareol with chromic acid mixture is simpler and more convenient[79,171]. A method analogous[170] to the direct oxidation of manoyl oxide to norambreinolide (173) [172] and a two-stage method via the aldehyde (175) (see Scheme 18)[64] have also been developed. The pathway involving the hydrogenolysis of manoyl oxide [or its epimer (15)] to dihydroabienol[64], which is oxidised to a mixture of compounds (173) and (174), is much more effective[62]. Although many sources of compounds (10) [3,75,95,96,173–178] and (15) [74,179–182] or their mixture[3,183–186] are known, so far only a few of them[187] are of preparative value.

Scheme 18



The mixture of compounds (173) and (174) is formed on ozonisation of 12α-hydroxy-13-epimanoyl oxide (176) [37] and in the multistage transformation of borjatriol (177),[188,189] which is a fairly readily available diterpenoid[190,191]. In principle, the familiar derivatives of the oxy-compounds (10) and (15) with oxygen-containing groups in the 2- and 3-positions[95], in the 3-position[192,193], in the 6-position[117], in the 11-position[176,177], in the 1- and 18-positions[194], and in the 3- and 18-positions[192] can serve as the starting materials for the synthesis of compounds (173) and (174).

In the synthesis of norambreinolide from the above diterpenoids the oxide (8) was found to be an intermediate. It is oxidised to the acetoxyacid (174), which gives rise to norambreinolide on intramolecular transesterification or after the elimination of acetic acid and cyclisation of the mixture of isomeric unsaturated acids (178) formed[162]. The acid (174) has been obtained from sclareol in two stages[195]. It is also formed in the ozonolysis of the oxide (8),[56] but the main product in this instance is the acetoxyaldehyde (125) [7,12] (see above), as in the study of Corey et al.[144]; the lactone (179) and the hydroxyacetate (124) are side products. The latter becomes the main product when the ozonide is reduced[7]. The hydrolysis of the acetoxyaldehyde (125) gives a mixture of sclaral (180) and the hydroxyacid (181). Oxidation can be avoided by carrying out the hydrolysis in an inert atmosphere or by protecting the aldehyde group[7]. The hydroxyaldehyde (180) exists in the form of the hemiacetal (182), which gives rise to a norambreinolide on oxidation[12]. The hemiacetal (182) has been discovered in tobacco[39] and has been suggested as an odorant for the latter[47]. The conversion of the oxide (8) into the acetoxyacid (174) on oxidation with a peracid is of interest[125].



The keto-oxide (183) is apparently converted analogously into the 3-oxoacetoxyacid (184) on treatment with Jones' reagent[65].

Norambreinolide can be conveniently synthesised from *cis*- and *trans*-abienols (185) and (186),[3] since it is the only product of their oxidation by different reagents[156,196,197]. In contrast to *trans*-abienol, the ozonisation of *cis*-abienol led to the peroxide (187) [198] (see Scheme 18). Abienols have been discovered in larches[3,183], for which they are taxonomic characteristics, in other conifers[75,174,180,186,199,200], and in tobacco[41,201]. In some of these plants the content of abienols is fairly high. Nevertheless, owing to their lability[156,202] and the lack of convenient methods for their isolation, abienols have not found practical applications. In particular, on heating *cis*-abienol isomerises to the neoabienols (27) and (28) [73] and it cannot therefore be isolated by distillation.

Norambreinolide is also formed on oxidation of α-levantenolide (188) [36] and the stereoisomeric oxides (189),[203] which are present in small amounts in tobacco.

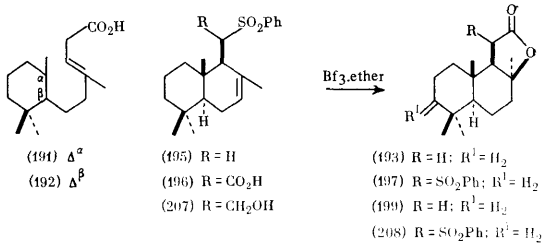
Racemic norambreinolide has been obtained by the cyclisation of homofarnesylic acid (190) [204] or α- and β-monocyclohomofarnesylic acids (191) and (192),[205–207] but the reaction products are complex mixtures of substances and the yield of the lactone (173) is low.

On treatment with acids, norambreinolide isomerises to 8-epinorambreinolide (193).[13,79,204,208] A stereospecific synthesis of this lactone has been achieved[209] as a result of the cyclisation of the sulphone (194) to drimenyl phenyl sulphone (195) [210,211] and the conversion of the latter into the acid (196), its transformation into the lactone (197), and desulphurisation. Compound (196) can be desulphurised and the resulting Δ^7-isomer of the acid (178) can then be converted into a lactone.

The ketoacid (184), whose hydrolysis gives rise to a mixture of the ketolactones (198) and (199), has been obtained from 3α-hydroxymanoyl oxide[65].

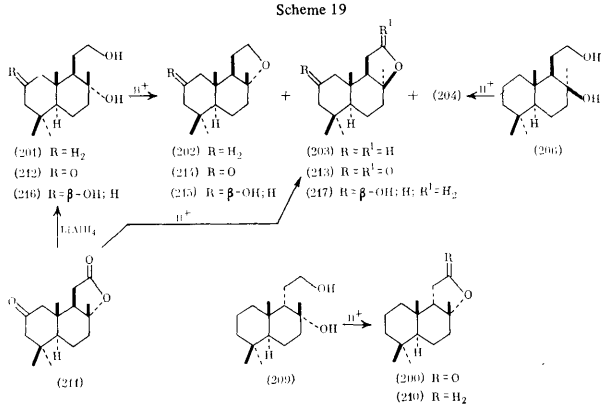
Hydrobromic acid[56] or a mixture of sulphuric and formic acids[207] isomerise the lactones (173) and (193) to the *cis*-lactone (200). Compounds (193) and (200) are also of interest for the synthesis of perfumes.

The diol (201) is formed on reduction of compounds (124), (125), (173), (174), and (179)–(181) with lithium tetrahydroaluminate[8,12,15,125] or on hydrolysis of the hydroxyacetate (124).[7] The possibility of the preparative reduction of norambreinolide with sodium in alcohol[15] has not been confirmed[32].



The diol (201) was obtained also in the reduction of the products of the ozonisation of the oxide (8) [6] and α-levantenolide[36]. In the former case a small amount of the oxide (202) was also isolated. The synthesis of the glycol (201) from the ketone (7), whereby manool can be converted into C_{16} compounds, has been described[83]: the ketone (7) is oxidised with a peracid to the epoxyacetate (162) and the latter is reduced.

Scheme 19



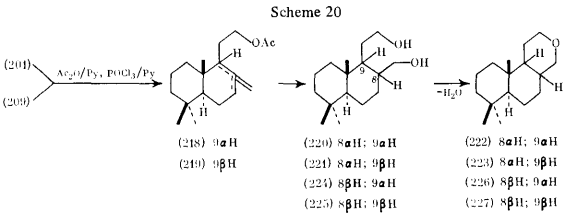
The dehydration of the diol (201) yields the oxides (202) and (203), a mixture of the isomeric alcohols (204), and a mixture of hydrocarbons whose structure has not been elucidated. The hydrocarbons have no odour, the alcohols (204) have a weak odour, while the oxide (203) and particularly the oxide (202) have a strong odour of ambergris and are of great value for the perfume industry. The dehydration of the glycol (201) has therefore been investigated in fair detail and it has been established that the ratio of the products depends on the catalyst and the reaction conditions. The oxide (202) predominates when the dehydration is carried out with naphthalene-β-sulphonic acids[7,14,15], toluene-*p*-sulphonic acid[208], sulphuric acid[32,62], alumina[8,14,15], and toluenesulphonyl chloride[62]. Alumina causes the simultaneous formation of a large amount of hydrocarbons, while toluene-*p*-sulphonic[171] and sulphuric acids give rise to a large amount of the alcohols (204). The latter predominate only on dehydration with dimethyl sulphoxide[212]. They can be obtained by reducing the mixture of the isomeric acids[178] produced by the pyrolysis[7,15] or treatment with sodium carbonate[48] of the acetoxyacid (174) of a mixture of its esters (205), which is a product of the interaction of norambreinolide with alcoholic solutions of acids[15,137,213]. The preparation of individual acid esters (205) [196] and the corresponding alcohols[94,212] has also been described. We may note that the oxide (202) is formed in the reduction of norambreinolide (173) with diborane, but its yield is low (~30%)[62].

If the diol (201) is dehydrated with hydrogen chloride, then the oxide (203) and a mixture of alcohols (204) predominate in the reaction products (see Scheme 19)[14,15,214]. This is also the case when the diol (206), formed by the reduction of the isolactone (193),[13] is dehydrated. Under the influence of acids, the oxide (202) isomerises to the epimer (203).[13] The stereospecific synthesis of the racemic oxide (203), in which the key stage is the cyclisation of the alcohol (207) to the tetrahydrofuran (208), has been achieved[209].

When the diol (209), produced by the reduction of the lactone (200), was dehydrated, the scented oxide (210) was obtained[215].

Like manoyl oxide, 2-oxomanoyl oxide or its ethylene ketal have been converted into compounds (211)–(214). On reduction, the last compound gives rise to the alcohol oxide (215).[63] When the ketolactone (211) is first reduced to the triol (216) and the latter is dehydrated, the yield of the oxide (215) is much lower. The reduction of the lactone (213) with diborane results in the formation of the alcohol oxide (217) (see Scheme 19). Compounds (210), (214), (215), and (217) have the odour of ambergris.

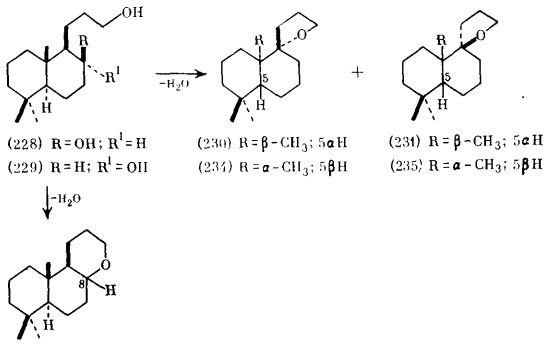
Scheme 20



The diols (201) and (209) have served as the starting materials for the synthesis of perhydronaphthopyran derivatives. They have been converted into mixtures of the acetates (218) and (219), in which the isomers with a semicyclic double bond predominate[216] (see Scheme 20). Their hydroboration led to the glycols (220) and (221), which can be dehydrated to the scented oxides (222) and (223).[217] On the other hand, if the mixture of the acetates (218) and (219) is epoxidised and the products isomerised by treatment with boron trifluoride etherate and reduced, the diols (224) and (225) are obtained[218]; on dehydration, these give rise to the oxides (226) and (227) with the odour of ambergris[219].

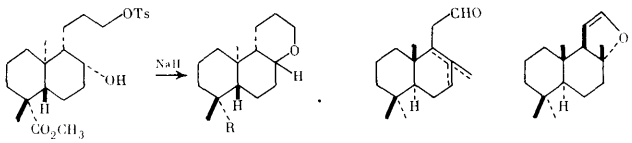
A series of oxy-derivatives of the labdane and *enantio*-labdane series have been described[50]. The reduction of the product of the ozonisation of podocarpenone leads to the epimeric glycols (228) and (229). The interaction of the former with toluene-*p*-sulphonic acid gives rise to a mixture of the spiro-oxides (230) and (231) while the corresponding reaction with the latter gives rise to the oxide (232). Compound (233) is the product of the dehydration of the glycol (228) with toluene-*p*-sulphonyl chloride. The syntheses of the enantiomeric compounds (234)–(236) have been achieved via the same scheme. The oxide (237) has been synthesised from the product of the cleavage of daniellic acid (238). The key stage in this synthesis is the formation of compound (239) on treatment of the hydroxytosylate (238) with sodium hydride (see Scheme 21).

Scheme 21



(228) R = OH; R¹ = H
(229) R = H; R¹ = OH
(230) R = β-CH₃; 5αH
(234) R = α-CH₃; 5βH
(231) R = β-CH₃; 5αH
(235) R = α-CH₃; 5βH
(232) 8βH
(233) 8αH

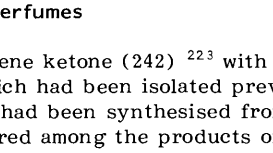
The vacuum distillation of the acetoxyaldehyde (125) leads to a mixture of unstable bicyclohomofarnesanes (240), which have been discovered in tobacco[43] and possess the odour of ambergris[7,12,220,221]. Their mixture as well as the individual γ-isomer are formed on oxidation of the corresponding alcohols[94,212]. The aldehydes (240) could not be obtained by the dehydration of the hydroxyaldehyde (180), since the latter dimerises on treatment with acids[12], but on vacuum distillation it is converted into a mixture of the aldehyde (240) and the oxide (241).[15] However, the attempts to obtain the hydroxyaldehyde (180) by oxidising the diol (201) [12,83,222] or by reducing norambreinolide[142] were unsuccessful, although 8-epinorambreinolide was reduced to the corresponding hydroxyaldehyde[142]. The reports that the γ-isomer of the aldehyde (240) is formed on oxidation of sclareol[16,19,32] were not confirmed[60].



(238)
(236) 8αH; R = CH₃
(237) 8βH; R = CH₃
(239) 8βH; R = CO₂CH₃
(240)
(241)

4. C_{15} and C_{14} Perfumes

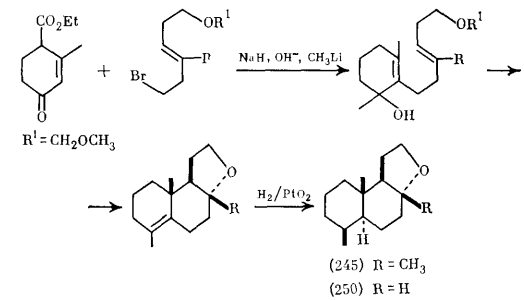
The sesquiterpene ketone (242) [223] with the odour of ambergris[224], which had been isolated previously from tobacco[43,225] and had been synthesised from drimenol (243),[225] has been discovered among the products of the oxidation of sclareol. However, it is much simpler to obtain it from a mixture of the esters (205). It is oxidised to the ketoester (244), whose hydrolysis yields the ketone (242).[226] If the mixture of the acids (178) is oxidised, the yield of the ketone (242) is lower[223]:



(243)
(242) R = CH₃
(244) R = CH₂CO₂CH₃

The scented noranalogue (245) of the oxide (202) without one methyl group at C(4) has been achieved recently[227] via Scheme 22.

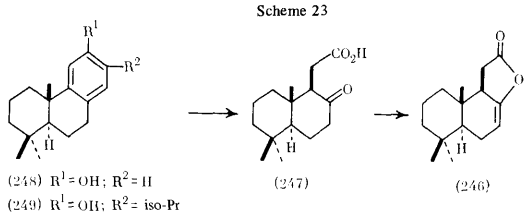
Scheme 22



(245) R = CH₃
(250) R = H

The enol lactone (246), synthesised together with its homologue (158) from certain labdanoids, has been recently used as an odorant for tobacco[48]. The corresponding keto-acid (247) was obtained from 12-hydroxypodocarpane (248) [228] and ferruginol (249) [229] (see Scheme 23), i.e. from readily available products of the conversion of resin acids.

Scheme 23

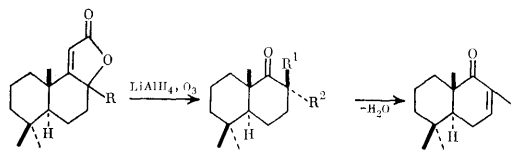


(248) R¹ = OH; R² = H
(249) R¹ = OH; R² = iso-Pr
(247)
(246)

The scented C_{14} analogue (250) of the oxide (202), lacking the methyl groups at C(4) and C(8), was also synthesised in accordance with Scheme 22.[227]

The scented ketone (251) has been found in the products of the oxidation of sclareol[123]. It had been synthesised earlier[46] from $\Delta^{9,11}$-dehydronorambreinolide (252) (Scheme 24), which had been obtained in its turn from norambreinolide[46,129] and has been recommended as a tobacco odorant. The synthesis of its C(8)-epimer (253) has also been described[129].

Scheme 24



(252) R = β-CH₃
(253) R = α-CH₃
(254) R¹ = CH₃; R² = OH
(255) R¹ = OH; R² = CH₃
(251)

On reduction with lithium tetrahydroaluminate and ozonisation, the lactones (252) and (253) give rise to the hydroxyketones (254) and (255). The lactone (252) can be converted into the hydroxyketone (254) by ozonisation and hydrolysis (223), but this procedure is less effective. The dehydration of the hydroxyketones (254) and (255) leads to the ketone (251).[129,223] The synthesis of the latter from drimenol is more complex[230].

IV. DEPENDENCE OF THE ODOUR OF PERFUMES OBTAINED FROM LABDANOIDS ON THEIR STRUCTURE

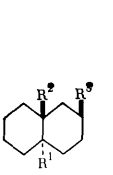
The question of the dependence of odour on the structure of substances is fairly complex and has not so far been solved. There does not exist a single theory of odour which would explain all the known facts and would have predictive

power. There is no objective criterion even for a qualitative estimation of odour. The human nose, capable of distinguishing several thousands of smells, is sufficiently sensitive, but the information obtained with its aid is to some extent subjective[231,232].

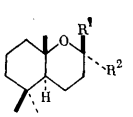
Two aspects of olfaction are distinguished: (1) the interaction of the molecules of the scented substance with the receptors of the olfactory nerve cells of the nasopharynx and (2) the transformation of the resulting primary excitation into a signal and its transmission to the olfactory brain hemisphere. The chemist is interested primarily in the way that the molecules of perfumes interact with the receptors of the olfactory nerve cells giving rise to the perception of a specific odour, i.e. how the structure of the given substance determines its odour[232].

Among the existing theories (more precisely hypotheses) of odour, the stereochemical theory of Amoore[233–235] has been most widely accepted; according to this theory, on the surface of the receptor there are alveoles of definite shape and size, each of which corresponds to a particular primary odour. Within the alveoles, there are strictly localised sections having an enhanced chamical affinity, which interact with the functional groups of scented substances. Consequently the odour is determined by the form of the molecule (or part of it) and by the nature and position of the functional groups. If the molecules of a given substance can be accommodated within an alveole of only one type, it possesses a primary odour and if it can be accommodated in alveoles of several types it has a complex odour.

Taking into account the structure of the perfumes (116), (117), (119)–(121), (202)–(204), and (240), Stoll[14,15] concluded that the odour of ambergris is characteristic of decalin derivatives of the type indicated with an oxygen-containing ring or a double bond at C(2) and an alcoholic or aldehyde group in the side chain. Compounds (52), (53), (71), and (72) as well as other substances with the same odour were discovered later. Ohloff[35] surveyed the data which had accumulated in the light of the sterochemical theory of odour and formulated the 1,2,4-triaxial rule. According to this rule, the odour of ambergris or any of its six constituent primary odours[53,236] is characteristic of compounds with a *trans*-decalin skeleton and three axial substituents (one of which can be an oxygen-containing group) located in the 1-, 2-, and 4-positions, as shown in formula (256), or molecules with a similar steric structure (or structural fragment), for example, tetrahydrochroman derivatives[129]: (52), (100), (109), (257), and (258). In the last case it is not essential that one of the substituents should contain oxygen. Incidentally, the nature of the substituent is not very important and affects only the shade or intensity of the odour. The data of Ohloff et al.[50] have shown that the oxygen-containing group need not necessarily be axial, provided that it is attached to a carbon atom with one more substituent. The environment of the centres responsible for the odour also does not play a special role. Indeed, despite structural changes, the oxides (163), (202), (214), (215), (245), and (250) and the ketals (52), (71), (72), (78), (81), (101), (102), (105)–(108), (164), and (165) have the odour of ambergris.

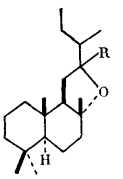


(256)



(257) $R^1 = CH_3$; $R^2 = H$

(258) $R^1 = CH_2{=}CH_2$; $R^2 = CH_3$



(259) R = α-H

(260) R = β-H

The π-electrons of the double bond or the keto-group can play the role of one of the axial substituents[35]. This explains the odour of compounds (119)–(121), (204), (240), (242), and (251), as well as a series of decalin derivatives with the keto-group at C(2).[237] Although compounds (53), (56), (92)–(96), (99), and (118) contain ketal and oxy-groups, they do not satisfy the triaxial rule and have no odour. Compounds (10), (15), and their derivatives, (259) and (260),[238] apparently have no odour owing to their high molecular weight.

The ambergris odour of *enantio*-labdane derivatives is as a rule weaker and has a different shade than that of their labdane enantiomers[50], which indicates yet again the chirality of the olfactory receptors and supports the stereochemical theory of odour.

However, a whole series of facts conflicting with the triaxial rule are known. Thus compounds (97), (98), (139), (171), (222), (223), (226), (227), and (233) do not satisfy its requirements but nevertheless have the odour of ambergris and conversely compounds (206), (168), (169), and many others, which do satisfy the requirements of the rule, nevertheless lack odour. If the environment of the centres responsible for the ambergris odour is not important, it is difficult to account for its disappearance on passing from the ketal (52) to its keto- and hydroxy-derivatives (57)–(59), on passing from the oxide (117) to its derivatives (113), (130), and (134)–(136), and also on conversion of compound (116) into compound (8), of compound (232) into compound (118), and of compound (52) into compound (65).

Thus small changes in the structure of the substance, which are insignificant from the standpoint of the triaxial rule, sometimes lead to unpredictable and inexplicable changes in odour or even to its disappearance. In view of the numerous exceptions, the rule so far lacks reliable predictive power and its value is reduced. Nevertheless it is already evident that odour is a property of the molecule as a whole and in this sense it should depend on its structure and stereochemistry. Further accumulation of factual data will probably help to elucidate the essential features of this dependence.

V. THE MANUFACTURE AND PRACTICAL APPLICATIONS OF PERFUMES BASED ON LABDANE DITERPENOIDS

As already mentioned, sclareol, manool, manoyl oxide, larixol, and others are quite readily available. This as well as the great value for perfumery of the compounds obtained from them having the odour of ambergris has made the synthesis of the latter not only of academic but also of practical interest. The method of synthesis of the oxide (202), known as "ambrox" and "ambroxide" from sclareol was the first to be patented[14,15]. Subsequently individual stages of its synthesis were frequently modified in order to adapt them to industrial conditions[20,32,171,208,239,240]. The industrially manufactured ambroxide and other products are mixtures of substances.

Simpler methods of synthesis of perfumes from sclareol and manool have also been developed. They consist in their oxidation by chromium(VI) compounds and the pyrolytic distillation of the oxidation products[16–18]. The method of preparation of this type of mixture of substances (ambrial) from sclareol was improved[19,32,33]. It was also shown that the distillation of the oxidation product can be replaced by its treatment with ascarite[34,241], although the nature of the perfumes is then altered[242]. However, their structure cannot be regarded as finally established, since it has been found[78] that the composition of the sclareol oxidation product

is in reality much more complex than had been previously believed[60].

The method of synthesis of the mixture of ketals (52) and (53) from manool has been reproduced under semi-industrial conditions[104].

Ambrial and ambroxide are used in the perfumery industry. Certain cleavage products of labdanoids are used to improve the quality of tobacco products. The following compounds have been patented for such purposes: (201), (202),[45] (173), (181), (252),[46] (180),[47] (158), and (246).[48]

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Very substantial advances have been made in the chemistry of perfumes bases on labdanoids. Several tens of substances with the odour of ambergris have been obtained from readily available diterpenoids (sclareol, manool, and others). The manufacture of some of these has been started. Interest in these compounds has been growing, because they have not only highly effective properties as perfumes but also possess a complex odour which embraces a fairly wide range of different shades.

During the last 10–15 years sources of new labdanoids, which can also be used in the syntheses of perfumes, have been discovered. The recently discovered method of introducing a double bond into the side chain of saturated labdanoids via organoselenium compounds leads to estensive possibilities. The search for perfumes based on *enantio*-labdane diterpenoids, already discovered in more than 30 plants, is promising. It is desirable to continue the study of the dependence of odour on structure since extensive factual data have been accumulated on these compounds; they also have a rigid carbon skeleton, which is very important in the solution of this problem. Finally, so far there are few methods of preparation of perfumes from labdane diterpenoids which are suitable for industrial applications.

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Transition Metal Complexes of Cyclopentadienylides and Pentafulvenes

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The π-complexes of cyclopentadienylides and pentafulvenes with six-electron coordination are examined. The question of the influence of the π-coordination with the transition metal atom on the properties of the cyclopentadienyl ring carrying a full or partial negative charge are discussed.
The bibliography includes 70 references.

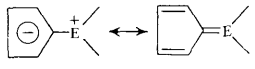
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I. INTRODUCTION

Complexes with cyclopentadienyl ligands are particularly widely represented among the π-complexes of transition metals. Typical examples of such compounds are ferrocene and cymantrene. The chemistry of these π-complexes has already developed extensively but some of their features have not been adequately explained. In particular, one of the cardinal problems remains obscure, namely how the properties and reactivity of the cyclopentadienyl anion change on π-coordination to the transition metal atom. The study of the properties of coordinated and non-coordinated cyclopentadienyl anions under comparable conditions involves considerable experimental difficulties. Fairly stable dipolar compounds, namely dicyclopentadienylides, in which the negative charge is distributed over the cyclopentadienyl ring linked to a heteroatom carrying a positive charge, as well as pentafulvenes, which are related to cyclopentadienylides, are therefore of great interest.

The structures of compounds of both types can be represented by two extreme forms: the ylide form (A) and the ylene form (B), whose contributions to the molecular structure depend significantly on the nature of the onium-forming atom E and the nature of the substitutents at this atom:



(A) (B)

In cyclopentadienylides the onium-forming atoms are usually those of Group V—VII elements. The contribution of structure (A) in such systems is fairly large. For example, the contribution of the ylide structure in triphenylphosphonium cyclopentadienylide $C_5H_4PPh_3$ exceeds 80%.[1] In pentafulvenes the atom E is carbon and the ylene structure (B) makes the greatest contribution. However, when powerful electron-donating groups with O, N, and S heteroatoms are attached to the exocyclic bond of the pentaulvenes, as, for example, in $C_5H_4CHN(CH_3)_2$, then pentafulvenes of this kind have large dipole moments and are characterised by a considerable contribution of the dipolar structure (A).

It has been found that cyclopentadienylides and pentafulvenes are capable of being coordinated to transition metal atoms, forming π-complexes. Thus it has been observed in 1959 [2] that the cyclopentadienyl fragment of triphenylphosphonium cyclopentadienylide is capable of being coordinated to Group VIB metal carbonyls as a six-electron ligand, forming π-cyclopentadienylide complexes.

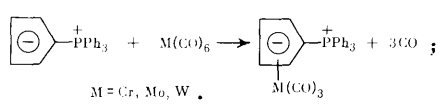
During the past 20 years, a wide variety of transition metal complexes have been synthesised, in which cyclopentadienylides and pentafulvenes play the role of π-ligands. However, hitherto there have been no surveys of cyclopentadienylide π-complexes in the literature (a review of fulvene complexes was published in 1970).[3] Presumably, examination of the literature data on transition metal π-complexes of cyclopentadienylides will make it possible to elucidate the nature of the influence of the π-coordination to the transition metal atom on the properties of the cyclopentadienyl ring carrying a full or partial negative charge. This review deals in detail only with the π-complexes of pentafulvenes in which they are coordinated to a transition metal atom as six-electron ligands. Such π-complexes of pentafulvenes are in many respects similar to the π-complexes of cyclopentadienylides and it is therefore of interest to compare the physical and chemical properties of complexes of the two types.

II. TRANSITION METAL COMPLEXES OF CYCLOPENTADIENYLIDES

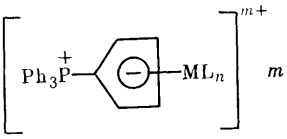
Group IV, VI, VII, and VIII transition metal π-complexes of phosphorus, sulphur, nitrogen, and arsenic cyclopentadienylides are known at present. All the complexes described in the literature are presented on page 660.

1. Synthesis

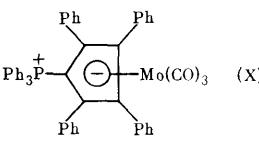
The complexes of cyclopentadienylides with metal carbonyls were first obtained by the reaction of triphenylphosphonium cyclopentadienylide with chromium, molybdenum, and tungsten hexacarbonyls in diglyme[2]:



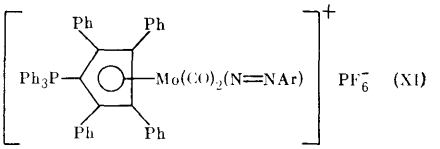
M = Cr, Mo, W.



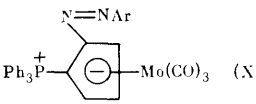
$m X^-$ (I)-(IX)



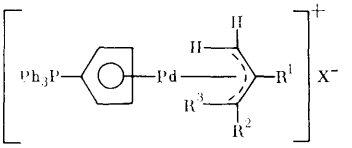
(X);



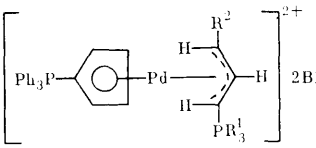
(XI)



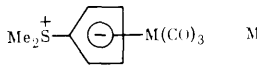
(XII);



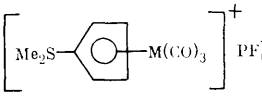
$R^1, R^2, R^3 = H$ or Me, $X = BF_4$ or CF_3SO_3 (XIII)-(XVIII);



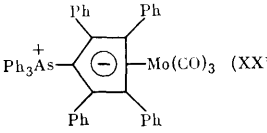
$2BF_4^-$ $R^1 = Et$ or Ph; $R^2 = H$ or Me (XIX)-(XXI);



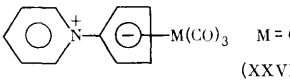
M = Cr, Mo, W (XXII)-(XXIV);



M = Mn, Re (XXV)-(XXVI)



(XXVII);



M = Cr, Mo

(XXVIII)-(XXIX)

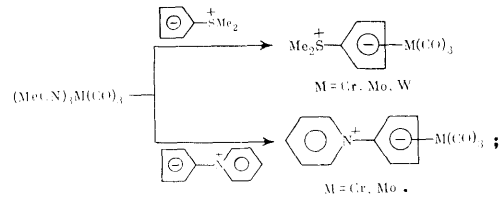
No.	ML_n		X^-
(I)	$Cr(CO)_3$	0	—
(II)	$Mo(CO)_3$	0	—
(III)	$W(CO)_3$	0	—
(IV)	$Mo(CO)_2(N{=}NAr)$	1	PF_6^-
(V)	$W(CO)_2(N{=}NAr)$	1	PF_6^-
(VI)	$Mo(CO)(PPh_3)(N{=}NAr)$	1	PF_6^-
(VII)	$Mn(CO)_3$	1	PF_6^-
(VIII)	$Re(CO)_3$	1	PF_6^-
(IX)	$Co(CO)_2$	1	$Co(CO)_4^-$

$(Ph_3PC_5H_4)_2WCl_6$ (XXX); $(Ph_3PC_5H_4)MoCl_3(CH_2$ (XXXI);
$[(Ph_3PC_5H_4)HgX_2]_2$ (X = Cl, Br, I) (XXXII) — (XXXIV);
$(Ph_3PC_5H_4)_2TiCl_4$ (XXXV); $(Ph_3PC_5H_4)TiCl_3$ (XXXVI);
$(Ph_3PC_5H_4)ZrCl_4$ (XXXVII); $(Ph_3PC_5H_4]HfCl_4$ (XXXVIII).

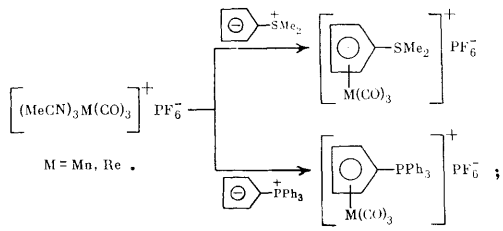
The yield of the complexes was up to 60%. Their compositions and structures were established by elemental analysis, infrared spectroscopy, and ^1H NMR. Subsequently a method of synthesis of cyclopentadienylide complexes from acetonitrile derivatives of Group VIB metal carbonyls was proposed[4]. Tetraphenyl-substituted triphenylphosphonium and triphenylarsonium cyclopentadienylidemolybdenum tricarbonyls have been obtained in high yields via the acetonitrile complex of molybdenum[5]. The attempt to obtain the molybdenum complex with stibonium cyclopentadienylide was unsucessful[5].

Complexes of dimethylsulphonium cyclopentadienylide with Group VIB metal carbonyls were obtained in 1974, also via the acetonitrile derivatives of the metals in diglyme[6,7] (yield up to 50%).

Complexes of pyridinium cyclopentadienylide with chromium and molybdenum carbonyls have been synthesised by an analogous method[8]. The tungsten analogue has not so far been obtained:

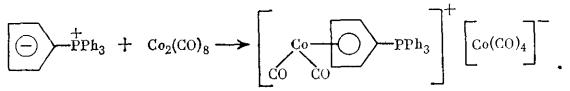


It has been found that, on treatment with charged acetonitrile complexes of manganese and rhenium, cyclopentadienylides form π-complexes with Group VII metal carbonyls[9,10].

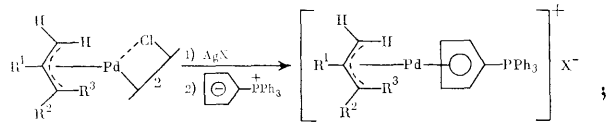


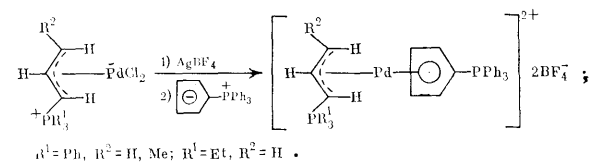
The reaction was carried out in tetrahydrofuran at room temperature in the case of the manganese complexes and with refluxing in the case of the rhenium complexes, the yields being 20–50%.

A report concerning the reaction of triphenylphosphonium cyclopentadienylide with cobalt carbonyl was published in 1978 [11]:



A series of palladium complexes containing triphenylphosphonium cyclopentadienylide as the π-ligand have been synthesised by the reaction of halogen-containing palladium compounds with cyclopentadienylide in the presence of silver salts[12]:





Reports of the synthesis of triphenylphosphonium cyclopentadienylide complexes with transition metal salts have appeared in the literature in recent years[13,14]. This ylide reacts with tungsten hexachloride in dry benzene[13]:

$$2Ph_3PC_5H_4 + WCl_6 \rightarrow (Ph_3PC_5H_4)_2WCl_6 .$$

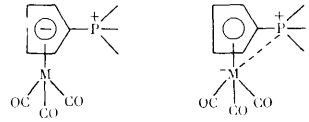
On the basis of ^1H and ^{13}C NMR spectra, the authors attribute a sandwich structure to the complex.

In an analogous reaction $MoCl_5$ gives rise to the complex $(Ph_3PC_5H_4)MoCl_3(OH)_2$, whose structure and authors do not discuss[14]. Complexes with mercury halides, namely $[Ph_3PC_5H_4HgX_2]_2$ (X = Cl, Br, or I), which are stable in air in the solid state, have also been obtained[14]; the complex with X = I has been comprehensively investigated.

Complexes of triphenylphosphonium cyclopentadienylide with titanium, zirconium, and hafnium salts have also been described: $(Ph_3PC_5H_4)_2TiCl_4$, $(Ph_3PC_5H_4)TiCl_3$, $(Ph_3PC_5H_4).ZrCl_4$, and $(Ph_3PC_5H_4)HfCl_4$.[15] The study of these complexes, which are very sensitive to atmospheric oxygen, involves considerable experimental difficulties; their structures have not so far been finally established. The authors[15], proposed the metallocene structure for $(Ph_3PC_5H_4)_2.TiCl_4$.

2. Structure

There have been two points of view concerning the structure of the π-complexes of phosphorus cyclopentadienylides with Group VIB metal carbonyls. On the one hand, such complexes have been treated as analogues of arenemetal tricarbonyls, assuming that the charges are neutralised in the ligand itself [structure (C)].[2] On the other hand, Cashman and Lalor[16] assumed that triphenylphosphonium cyclopentadienylide complexes are similar to cyclopentadienylmetal tricarbonyl anions $[C_5H_5M(CO)]_3^-$ (M = Cr, Mo, or W) and are stablised by the interaction of one of the filled non-bonding metal orbitals with the vacant *d* orbital of the phosphorus atom [structure (D)]:



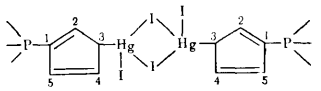
(C) M = Cr, Mo, W. (D)

However, X-ray diffraction analysis of dimethylsulphonium cyclopentadienylide and its π-complexes with chromium and molybdenum carbonyls[17,18] showed that the chromium atom in dimethylsulphonium cyclopentadienylidechromium tricarbonyl is symmetrically coordinated (by an octahedron) with the cyclopentadienyl ring (three coordination sites) and with three carbonyl groups. The distance between the sulphur and chromium atoms (3.478 Å) greatly exceeds the sum of the covalent radii of the chromium and sulphur atoms (2.52 Å). The absence of the Cr...S interaction is also indicated by the deviation of the S atom from the plane of the cyclopentadienyl ring by 0.110 Å towards the opposite chromium atom.

Comparison of the structural parameters of dimethylsulphonium cyclopentadienylide and its π-complex with chromium showed that the π-coordination to the transition metal is not accompanied by sharp changes in the structure of the cyclopentadienylide but leads to an increase of the contribution of the ylide structure. For example, the C–C bond lengths in the cyclopentadienyl ring of the π-complex are somewhat more equalised than in the initial cyclopentadienylide, while the partial double bond character of the sulphur–cyclopentadienyl ring bond is more pronounced in the ylide than in the complex.

The X-ray diffraction analysis of the complex of triphenylphosphonium cyclopentadienylide with cobalt carbonyl was carried out in 1978.[11] The authors noted that the structure of this cationic complex resembles that of the complex of dimethylsulphonium cyclopentadienylide with chromium carbonyl. On the other hand, there is similarity with the $C_5H_5Co(CO)_2$ structure.

The complex of triphenylphosphonium cyclopentadienylide with mercury iodide has a different structure[14]. In the solid state the complex exists as a dimer with two bridging iodine atoms:



The mercury atom is linked by a π-bond to the C(3) carbon atom of the five-membered ring of the ylide. The C(1)–C(2) and C(4)–C(5) bonds are appreciably shorter than the other bonds, which indicates their double bond character. From the ^{13}C NMR spectrum, the authors assume that in solution the mercury atom is linked alternately to the C(2), C(3), C(4), and C(5) atoms.

3. Physicochemical Properties

The complexes of cyclopentadienylides with metal carbonyls are solid crystalline substances. With the exception of pyridinium cyclopentadienylide complexes, they are relatively resistant to the action of atmospheric oxygen. In the solid state the complexes decompose slowly in air, but their solutions are relatively unstable.

Table 1. Parameters of the infrared and ^1H NMR spectra of complexes of cyclopentadienylides.

Cpd.	i.r. spectra			^1H NMR spectra		
	ν(C≡O), cm^{-1}	solvent*	refs	δ(C_5H_5), p.p.m.	solvent	refs
(I)	1913; 1806	$CHCl_3$	[4]	4.92; 4.65	$CHCl_3$	[4]
(II)	1920; 1812	$CHCl_3$	[4]	5.49; 5.23	$CHCl_3$	[4]
(III)	1912; 1802	$CHCl_3$	[4]	5.49; 5.22	$CHCl_3$	[4]
(IV)	1997; 1925	(KBr)	[5]	—	—	—
(V)	1993; 1909	(KBr)	[5]	—	—	—
(VI)	1892	(KBr)	[5]	—	—	—
(VII)	2040; 1963	acetone	[10]	5.83	$(CD_3)_2CO$	[10]
(VIII)	2038; 1950		[10]	6.27	$(CD_3)_2CO$	[10]
(IX)	2109;2082;1890	(KBr)	[11]	—	—	—
(X)	1920; 1813	CH_2Cl_2	[5]	—	—	—
(XI)	1993; 1926	(KBr)	[5]	—	—	—
(XII)	1924; 1830; 1819	(KBr)	[5]	—	—	—
(XIII)	—	—	—	6.33	$CDCl_3$	[12]
(XIX)	—	—	—	6.05; 5.60; 5.75	$CDCl_3$	[12]
(XXII)	1920; 1820	acetone	[19]	5.29; 4.69	$(CD_3)_2SO$	[19]
(XXIII)	1925; 1825	acetone	[19]	6.09; 5.47	$(CD_3)_2SO$	[19]
(XXIV)	1915; 1820	acetone	[19]	5.92; 5.33	$(CD_3)_2SO$	[19]
(XXV)	2042; 1963	acetone	[10]	6.23; 5.47	$(CD_3)_2CO$	[10]
(XXVI)	2022; 1940	acetone	[10]	6.90; 6.15	$(CD_3)_2CO$	[10]
(XXVII)	1919; 1814	CH_2Cl_2	[5]	—	—	—
(XXVIII)	1920; 1820	acetone	[8]	5.55; 4.63	$(CD_3)_2CO$	[8]
(XXIX)	1920; 1820	acetone	[8]	6.20; 5.30	$(CD_3)_2CO$	[8]
(XXX)	—	—	—	8.57	MeCN	[13]
(XXXII)	—	—	—	6.33—6.72	$CDCl_3$	[14]
(XXXV)	—	—	—	7.95	Me_2SO	[15]

*The material used for pressing the specimen discs is indicated in brackets.

(a) *Infrared and NMR spectra.* The parameters of the infrared and ^1H NMR spectra of the cyclopentadienyl complexes of metal carbonyls are presented in Table 1. Evidently, the infrared spectra of these complexes are characterised by intense absorption bands in the region of the vibration frequency of the terminal CO groups. Two signals due to the protons of the five-membered ring and the multiplet due to the protons of the benzene rings can be observed in the ^1H NMR spectra of triphenylphosphonium cyclopentadienylide complexes with Group VIB metal carbonyls. In these complexes the metal is coordinated to the five-membered and not the six-membered ring of the ylide since the signals of the protons in the five-membered ring of the complexes are displaced upfield, relative to the initial ylide, while the chemical shifts of the protons in the benzene rings hardly charge on formation of the complexes[2].

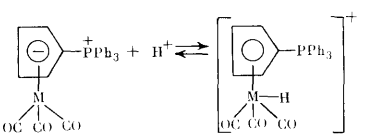
The most interesting information about the influence of coordination to the metal on the physicochemical properties of cyclopentadienylides has been obtained in the study of the ^{13}C NMR spectra[10,20]. Comparison of the $^{13}C\{^1H\}$ spectra of triphenylphosphonium and dimethylsulphonium cyclopentadienylides and their complexes with Group VIB metal carbonyls showed that the π-coordination to the $M(CO)_3$ group (M = Cr, Mo, or W) leads to an appreciable equalisation of the electron density in the five-membered ring of the coordinated cyclopentadienylide[20].

It has also been shown[20] that the shielding of the nuclei of all the carbon atoms of the cyclopentadienyl fragment of the ligand increases on π-coordination, the degree of shielding depending on the nature of the central metal atom and varying in the sequence Cr > W > Mo.

(b) *Electrical conductivity and degree of dissociation.* The complexes of cyclopentadienylides with Group VII and VIII metals are saltlike compounds. Solutions of complexes of triphenylphosphonium and diphenylsulphonium cyclopentadienylides with manganese and rhenium carbonyls in acetone conduct electricity; the molar conductances Λ_M are close to the average value for binary electrolytes formed by coordination compounds[10]. The degrees of dissociation α of these complexes in solution have been calculated from the molecular weights determined ebullioscopically in ethyl methyl ketone[10]. Comparison of the values of α for different complexes showed that the cyclopentadienylide complexes of rhenium are weaker electrolytes than the analogous manganese compounds and that, for the same central metal atom, the triphenylphosphonium cyclopentadienylide complexes are more dissociated in solution than the dimethylsulphonium cyclopentadienylide complexes. The electrical conductivities of the saltlike complexes of palladium with triphenylphosphonium cyclopentadienylide have also been measured[12], but the results are not discussed by the authors.

4. Chemical Properties

(a) *Protonation.* It was shown in 1970 that the complexes of triphenylphosphonium cyclopentadienylide with chromium, molybdenum, and tungsten carbonyls dissolve rapidly in trifluoroacetic acid, forming pale-blue solutions. The infrared and ^1H NMR spectra of the solutions (Table 2) indicate the reversible protonation of the complexes at the metal atom:



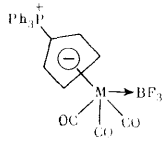
Thus the high-field signal (δ in the range between −5 and −8 p.p.m.) in the ^1H NMR spectra of these solutions is characteristic of the proton linked to the metal atom, as in the corresponding hydrides $C_5H_5M(CO)_3H$. The signal of this proton in the spectrum of the tungsten complex is split owing to the interaction with the ^{183}W nucleus; the spin–spin coupling constant (36 Hz) is close to the value of $J_{^{183}W-^1H}$ for $C_5H_5W(CO)_3H$ and $[(C_5H_5)_2W_2(CO)_6H]^+$.

The stretching vibration frequencies of the carbonyl groups of the protonated complexes were found to have undergone a hypsochromic shift relative to the non-protonated complexes by more than 100 cm^{-1} (Table 2). This fact indicates an increase of the C–O bond order in the protonated complexes as a consequence of the appearance of a positive charge on the metal atom. The study of the parameters of the ^1H NMR spectra of the protonated complexes of triphenylphosphonium cyclopentadienylide with various central metal atoms showed[14] that the basicity of the cyclopentadienylide complexes of Group VIB metals increases with increase of the atomic weight of the metal.

Table 2. Parameters of the ^1H NMR and infrared spectra of the protonated complexes $[(Ph_3PC_5H_4)M(CO)_3H]^+$.[4]

M	δ(C_5H_4), p.p.m.	δ(M–H), p.p.m.	ν(C≡O), cm^{-1}
Cr	5.42; 5.20	−5.09	2042; 1962
Mo	5.91; 5.69	−5.34	2048; 1970
W	6.00; 5.73	−7.15	2042; 1958

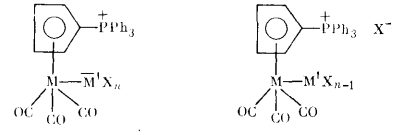
(b) *The formation of adducts with Lewis acids.* The cyclopentadienylide complexes of Group VIB metals form adducts with Lewis acids. Triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl and its tungsten analogue form solid dark-red adducts with BF_3, which have been investigated by elemental analysis and infrared spectroscopy[4]:



M = Mo, W.

The chromium complex also reacts with BF_3, but the adducts could not be isolated in a solid state owing to their dissociation. The boron trifluoride in these adducts forms a bond with the metal, which follows from the infrared spectra; the basicity of the complexes relative to BF_3 increases with increase of the atomic number of the metal.

A study has also been made of the interaction of triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl and its tungsten analogue with other Lewis acids: CdI_2, $HgCl_2$, $HgBr_2$, HgI_2, $GaBr_3$, and $InBr_3$.[5] The products were 1:1 adducts, moderately resistant to the action of air but sensitive to light. No 1:2 adducts were detected although an excess of Lewis acids was used. Since all the vibration frequencies of the carbonyl groups of the adducts have undergone a bathochromic shift relative to the initial complexes, it was concluded that the central metal atom is the site of attack by the Lewis acid. The authors[5] were unable to make a choice between two structures of the adducts:



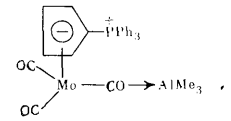
M = Mo, W $\quad$ $M'X_n$ = CdI_2, $HgCl_2$, $GaBr_3$ etc.

They believe that the ready formation of the adducts indicates the presence of a negative charge on the metal atom in the cyclopentadienylidemetal tricarbonyl complexes and also that the interaction of the metal with the phosphonium centre in these complexes is weak and does not prevent the reaction with the Lewis acid.

The study of the reactions of Group VIB metal complexes of triphenylphosphonium cyclopentadienylide in methylene chloride with strong Lewis acids such as $AlCl_3$ and $TiCl_4$[21] also demonstrated the occurrence of interaction via the metal atom.

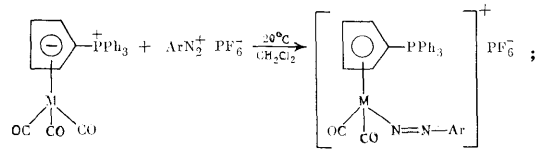
The formation of an adduct via the metal atom between triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl and liquid SO_2 has been decribed[5].

In contrast to the interaction with Lewis acids described above, trimethylaluminium reacts with triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl to form an adduct having a different structure[22]:



Tensimetric titration of the resulting compound with trimethylamine indicates the formation of a 1:1 adduct. The infrared spectrum contains bands at 1932, 1845, and 1665 cm^{-1} in the region corresponding to the vibrations of the CO group. Thus the stretching vibration frequencies of one CO group diminish markedly (by more than 100 cm^{-1}) due to the coordination to $AlMe_3$, while the stretching vibration frequencies of the two non-coordinated CO groups increase by ~15–30 cm^{-1}.

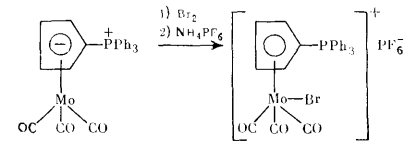
(c) *Reactions with arenediazonium salts.* *p*-Methoxybenzenediazonium hexafluorophosphate readily reacts with molybdenum and tungsten complexes of triphenylphosphonium cyclopentadienylide, giving rise to quantitative yields of products of the substitution of one carbonyl groups by the areneazo-group[5]:



M = Mo, W; Ar = *p*-$MeOC_6H_4$.

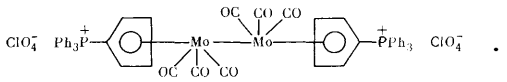
The corresponding chromium complex decomposes under the same conditions. The reaction is analogous to that of $[C_5H_5Mo(CO)_3]^-$ with $ArN_2^+X^-$.[5]

(d) *Reactions with halogens.* Triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl reacts with chlorine, bromine, or iodine at room temperature, the halogen adding to the metal[5]:

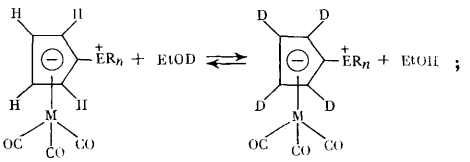


The reaction takes place more smoothly when the intial complex (or its tungsten analogue) is treated with carbon tetrachloride or tetrabromide in CF_3COOH. The halogen adds to the metal atom of the complex $(Ph_3PC_5H_4)Mo(CO)_3$ also on treatment with $SbCl_5$ or $C_5H_5Co(CO)I_2$.[5]

(e) *Oxidation.* The effect of one-electron oxidants, namely tri(*p*-bromophenyl) ammonium salts, has been investigated in relation to the molybdenum complex of triphenylphosphonium cyclopentadienylide[5]. Treatment with $[(BrC_6H_4)_3N]^+ \cdot [SbCl_6]^-$ results in the formation, analogously to the reaction involving halogens, of the salt $[Ph_3PC_5H_4Mo(CO)_3Cl]^+ \cdot [SbCl_6]^-$. On the other hand, on treatment with the substituted ammonium perchlorate, the complex is oxidised with formation of a dimer:



(f) *Hydrogen isotope exchange.* It has been recently observed that the complexes of cyclopentadienylides with Group VIB metal carbonyls can undergo the hydrogen isotope exchange (HIE) reaction with deuteroethanol in neutral media [19,23]:



M = Cr, Mo, W; ER_n = Me_2S, Ph_3P.

Table 3. The rate constant for hydrogen isotope exchange involving cyclopentadienylides and their π-complexes with Group VIB metals (in acetone at 50 °C).[19,23]

Compound	k, s^{-1}	Compound	k, s^{-1}
$(Me_2SC_5H_4)$	$7.0 \cdot 10^{-5}$	$Ph_3PC_5H_4$	$6.7 \cdot 10^{-5}$
$(Me_2SC_5H_4)Cr(CO)_3$	$2.1 \cdot 10^{-7}$	$(Ph_3PC_5H_4)Cr(CO)_3$	No exchange
$(Me_2SC_5H_4)Mo(CO)_3$	$2.9 \cdot 10^{-5}$	$(Ph_3PC_5H_4)Mo(CO)_3$	$8.2 \cdot 10^{-6}$
		$(Ph_3PC_5H_4)W(CO)_3$	$7.1 \cdot 10^{-7}$

The authors used the hydrogen isotope exchange method to compare the reactivities of cyclopentadienylide complexes containing various metals and various onium atoms. Table 3 presents the rate constants for the HIE of cyclopentadienylides and their π-complexes with EtOD in acetone. The results show that the influence of π-coordination to a transition metal on the reactivity of cyclopentadienylides is determined to a large extent by the nature of the central metal atom. For example, the rate constants for the hydrogen isotope exchange under identical conditions are similar in magnitude for dimethylsulphonium cyclopentadienylide and its π-complex with $Mo(CO)_3$, whereas the rate constants for triphenylphosphonium cyclopentadienylide and its complex with $Mo(CO)_3$ differ only by an order of magnitude. On the other hand, the influence of π-coordination to the $Cr(CO)_3$ group is manifested much more intensely and the rate of HIE involving the chromium complex of dimethylsulphonium cyclopentadienylide diminishes by a factor greater than two compared with the non-coordinated ylide. The $W(CO)_3$ group occupies an intermediate position between $Cr(CO)_3$ and $Mo(CO)_3$ as regards its influence on the HIE of cyclopentadienylides.

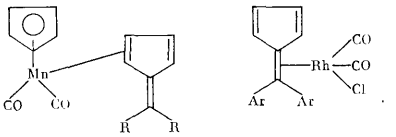
Thus the reactivity of the cyclopentadienyl ring in isotope exchange between cyclopentadienylides and their π-complexes with Group VIB metal carbonyls varies in the sequence S- or P-cyclopentadienylide ≧ Mo complex of ylide > W complex of ylide > Cr complex of ylide.

It has also been shown for the π-complex of dimethylsulphonium cyclopentadienylide with $Mo(CO)_3$ [20] that the π-coordination to the transition metal leads to the abolition of the differences between the rates of exchange in the α- and β-positions of the five-membered ring of the π-ligand, in contrast to the non-coordinated cyclopentadienylide, where the α-position is more reactive.

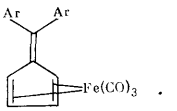
III. TRANSITION METAL COMPLEXES OF PENTAFULVENES

Pentafulvenes can be coordinated to transition metals in various ways:

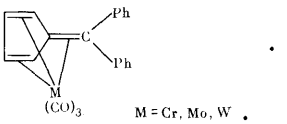
1. Via one double bond[25,27]:



2. Via two double bonds[26]:

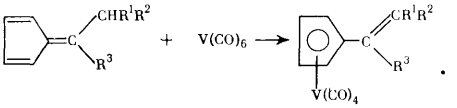


3. Via three double bonds[28,40]:

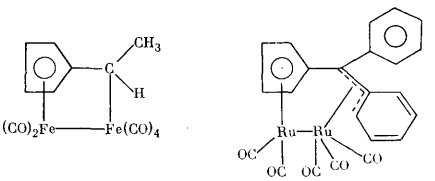


M = Cr, Mo, W.

4. To the cyclopentadienyl ring as the donor of five electrons[29]:

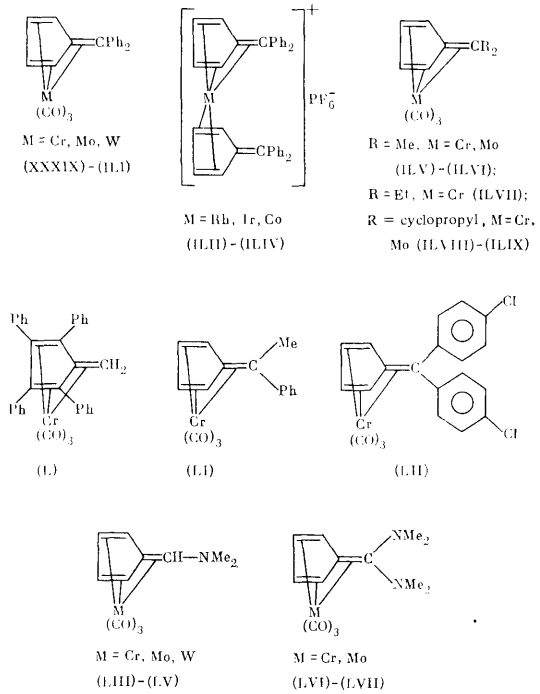


5. In a complex manner[30,31]:



Pentafulvenes are structural units of molecules of compounds such as calicenes, fulvalenes, azulenes, etc. Some of these compounds form complexes with transition metals; for example, the complex of azulene with $Cr(CO)_3$ was described in 1978.[24] However, in this review we shall not consider the complexes of such compounds. We shall deal only with the complexes of pentafulvenes in which the coordination to the metal takes place via three double bonds of the pentafulvene, i.e. the pentafulvene is a six-electron ligand. Such π-complexes of pentafulvenes are comparable

to the π-complexes of cyclopentadienylides with metal carbonyls. All the pentafulvenes with six-electron coordination described in the literature hitherto are presented below:



M = Cr, Mo, W (XXXIX)-(XLI)

M = Rh, Ir, Co (XLII)-(XLIV)

R = Me, M = Cr, Mo (XLV)-(XLVI); R = Et, M = Cr (XLVII); R = cyclopropyl, M = Cr, Mo (XLVIII)-(XLIX)

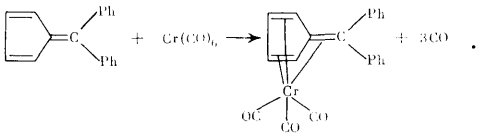
(L) (LI) (LII)

M = Cr, Mo, W (LIII)-(LV)

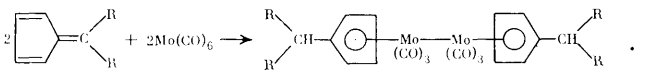
M = Cr, Mo (LVI)-(LVII)

1. Synthesis

The complex of 6,6-diphenylfulvene with chromium carbonyl was first obtained in 1961 by the reaction of fulvene with $Cr(CO)_6$ in hydrocarbon solvents[32]:

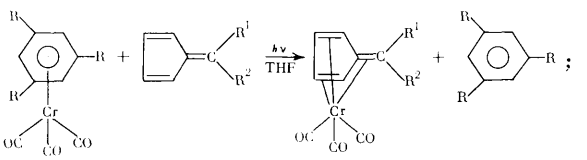


The analogous reactions of the metal carbonyls $Mo(CO)_6$ and $W(CO)_6$ with pentafulvenes in solvents of the type of ethers or in the absence of a solvent form only dimeric complexes (with breakdown of the fulvene structure)[33,34]:



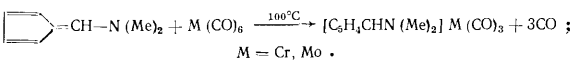
However, it was shown in 1977 that the reactions of 6,6-dialkyl- and 6,6,-diarylpentafulvenes with acetonitrile derivatives of chromium, molybdenum, and tungsten carbonyls in tetrahydrofuran (THF) lead to the formation of fulvene complexes in the case of all three metals[28].

It has been found recently that pentafulvene can substitute the π-arene ligand in arenechromium tricarbonyl complexes with formation of pentafulvene complexes[35]:



R = H, Me; R^1 = Me, R^2 = Ph; $R^1 = R^2 = C_6H_4Cl$.

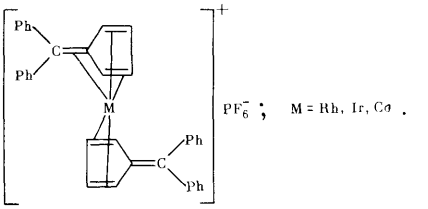
Complexes of 6-(*N*,*N*-dimethylamino)- and 6,6-bis(*N*,*N*-dimethylamino)-fulvenes with chromium and molybdenum carbonyls can be obtained by the direct reaction of the fulvenes with $Cr(CO)_6$ and $Mo(CO)_6$ in cyclohexane[36]:



M = Cr, Mo.

Under these conditions, $W(CO)_6$ does not react with 6-(*N*,*N*-dimethylamino)fulvene and the acetonitrile derivative of tungsten is used to obtain the fulvene complex[37].

Sandwich complexes of 6,6-diphenylfulvene with rhodium, iridium, and cobalt salts were obtained[38] as early as 1967:

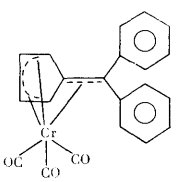


These charged complexes were obtained by the reaction of 6,6-diphenylfulvene, the metal salt, and isopropylmagnesium bromide followed by ultraviolet irradiation, hydrolysis of the reaction mixture, and oxidation with atomospheric oxygen. The yield of the complexes is very low: 6, 0.8, and 0.04% in the case of $CoCl_2$, $RhCl_3$ and $IrCl_3$ respectively. Only charged biscyclopentadienyl complexes of the metals have been isolated after the analogous reaction of 6,6-dimethylfulvene with $RhCl_3$ and $CoCl_2$, i.e. the fulvene structure of the ligand decomposed as a result of the addition of hydrogen to the exocyclic double bond.

2. Structure

It was postulated previously[32] that in the reaction of 6,6-diphenylfulvene with chromium carbonyl the complex formation process involves the benzene ring of the fulvene. However, later the same investigators[39] established by ^1H NMR that the five-membered and not the six-membered ring of 6,6-diphenylfulvene is coordinated to the chromium atom.

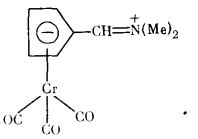
Complete X-ray diffraction analysis of 6,6-diphenylfulvene chromium tricarbonyl confirms the coordination to the five-membered ring[40,41]. It was shown that in the molecule of the complex the chromium atom is linked to all six carbon atoms of the pentafulvene ligand and to the three carbonyl groups, assuming a distorted octahedral coordination. The planarity of the fulvene system is then appreciably disturbed as a result of the deviation of the exocyclic carbon atom towards the chromium atom. Thus the coordination of the chromium atom in 6,6-diphenylfulvenechromium tricarbonyl can be represented as coordination to the butadiene system of the cyclopentadienyl ring and to the exocyclic double bond of the fulvene:



Theoretical analysis[42] of the preferred conformation of the complex (fulvene)$Cr(CO)_3$ showed that the calculated angle of the deviation of the exocyclic carbon atom from the plane of the five-membered ring is close to the experimental value[41].

Comparison of the structure of 6,6-diphenylfulvenechromium tricarbonyl with that of dimethylsulphonium cyclopentadienylidechromium tricarbonyl shows that they differ sharply. In the case of the fulvene complex the exocyclic carbon atom is involved in coordination to the metal, while in the case of the cyclopentadienylide complex the sulphur atom is displaced from the plane of the five-membered ring in the direction opposite to that of the chromium atom and is not linked to the latter.

From X-ray diffraction data for 6-(*N*,*N*-dimethylamino)-fulvenechromium tricarbonyl, it has been concluded[43] that the molecule of this complex contains the fulvene ligand in a dipolar form stabilised by the complex formation reaction between the negatively charged five-membered ring and the $Cr(CO)_3$ group. Thus it has been shown that complex formation results in a significant equalisation of the C–C bond lengths in the cyclopentadienyl ring of the ligand and an increase of the multiplicity of the bond between the nitrogen atom and the exocyclic carbon atom:



3. Infrared and NMR Spectra

The infrared spectra of the metal carbonyl complexes of pentafulvenes with six-electron coordination are characterised by intense absorption bands in the same region of absorption by terminal CO groups as in the spectra of the metal carbonyl complexes of cyclopentadienylides (Table 4). The ^1H NMR spectra of pentafulvene complexes (Table 4) exhibit under the usual conditions two signals due to the α- and β-protons of the five-membered ring, the signals having undergone an upfield displacement relative to the non-coordinated pentafulvene, as in the case of the cyclopentadienylide π-complexes.

The study of the ^{13}C NMR spectra of the chromium tricarbonyl complexes of 6,6-diphenylfulvene and 6-(*N*,*N*-dimethylamino)fulvene[44] showed that the π-coordination of pentafulvenes to the $Cr(CO)_3$ group is accompanied by an increase of the energy of the shielding of the nuclei of all the carbon atoms of the cyclopentadienyl ring, as in the cyclopentadienylide complexes, the effect being observed to a more marked extent in systems with a more pronounced ylene structure. It has also been found that the coordination of 6,6-diphenylfulvene to the chromium atom entails an appreciable increase of the shielding of the exocyclic carbon atom (there is an upfield shift of the signal due to the ^{13}C atom by 26 p.p.m.), while the coordination of 6-(*N*,*N*-dimethylamino)fulvene to the $Cr(CO)_3$ group is accompanied by the deshielding of the exocyclic carbon atom (there is a downfield shift of the signal due to the ^{13}C atom by 6 p.p.m.). The authors[44] explained these facts by a difference between the structures of the complexes. According to X-ray diffraction analysis, the exocyclic double bond of 6,6-diphenylfulvene is involved in coordination to the chromium atom, which leads to an increase of the shielding of the nuclei of the carbon atoms in this bond. On the other hand, if the coordination of 6-(*N*,*N*-dimethylamino)fulvene to the $Cr(CO)_3$ group is accompanied by an increase of the contribution of the ylide structure, one would expect the deshielding of the nucleus of the C_{ex} atom adjoining the onium nitrogen atom and also an increase of the barrier to rotation about the $C_{ex}=N^+Me_2$ bond. The authors found confirmation of this hypotheis in the observation that, apart from the deshielding of the $^{13}C_{ex}$ nucleus, two signals also appear in the ^{13}C NMR spectra due to the CH_3 groups at the nitrogen atom (in contrast to the initial fulvene). The hypothesis of an increase of the contribution of the ylide structure on π-coordination of 6-(*N*,*N*-dimethylamino)fulvene to $Cr(CO)_3$, based on the study of the ^{13}C NMR spectra, was subsequently confirmed by X-ray diffraction[43].

4. Chemical Properties

The chemical properties of the π-complexes of pentafulvenes have been studied extremely little. It has been shown[39] that 6,6-diphenylfulvenechromium tricarbonyl is readily reduced by sodium tetrahydroborate with formation of an anionic cyclopentadienyl complex of chromium:

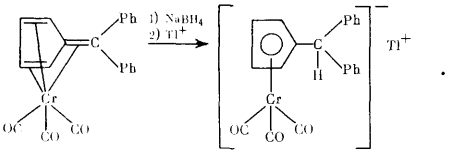
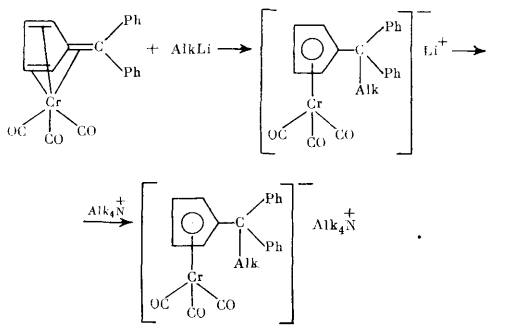


Table 4. Parameters of the infrared and ^1H NMR spectra of π-complexes of pentafulvenes with six-electron coordination.

Compound	i.r. spectra		^1H NMR spectra		
	ν(C≡O), cm^{-1}	refs	δ(C_6H_6), p.p.m.	solvent	refs
(XXXIX)	1971; 1907; 1886	[28]	4.60; 4.18	C_6D_6	[28]
(IL)	1974; 1901; 1885	[28]	4.77; 4.53	C_6D_6	[28]
(ILI)	1969; 1882; 1874	[28]	5.60; 5.05	$CDCl_3$	[28]
(ILII)	—	—	5.0; 4.68; 4.3	SO_2 (liq.)	[38]
(ILIV)	—	—	4.79; 4.37; 4.21	SO_2 (liq.)	[38]
(ILV)	1975; 1908; 1880	[28]	4.67; 3.98	C_6D_6	[28]
(ILVI)	1981; 1909; 1875	[28]	4.88; 4.41	C_6D_6	[28]
(ILVII)	1989; 1898	[28]	4.68; 3.98	C_6D_6	[28]
(ILVIII)	1954; 1894; 1863	[28]	4.79; 4.44	C_6D_6	[28]
(ILIX)	1950; 1895	[28]	5.74; 5.23	$CDCl_3$	[28]
(L)	1984; 1919; 1890	[28]	—	—	—
(LI)	1971; 1893	[35]	5.26; 4.60	$CDCl_3$	[35]
(LII)	1985; 1907	[35]	5.44; 4.67	$CDCl_3$	[35]
(LIII)	1909; 1820; 1788 *	[36]	5.09	$(CD_3)_2CO$	[36]
(LIV)	1908; 1815; 1785 *	[36]	5.66; 5.51	$(CD_3)_2CO$	[36]
(LV)	1906; 1810; 1787 *	[37]	—	—	—
(LVI)	1914; 1799; 1777 *	[36]	—	—	—
(LVII)	1914; 1803; 1783 *	[36]	—	—	—

*The infrared spectra were recorded in liquid paraffin; in the remaining cases the spectra were measured using discs with KBr.

An analogous reaction involving the nucleophilic addition of alkyl-lithium was described in 1977 [28]:



The hydrogen isotope exchange involving the molybdenum complex of 6-(*N*,*N*-dimethylamino)fulvene on treatment with deuteroethanol in a neutral medium has been studied recently under the same conditions as for the corresponding molybdenum complexes of triphenylphosphonium or dimethylsulphonium cyclopentadienylide[20]. It has been shown that the rate of isotope exchange in ylide–ylene systems coordinated to a transition metal atom increases with increase of the contribution of the ylide form to the structure of the ligand:

$$[Me_2NCHC_5H_4]Mo(CO)_3 < (Ph_3PC_5H_4)Mo(CO)_3 < [Me_2SC_5H_4]Mo(CO)_3 .$$

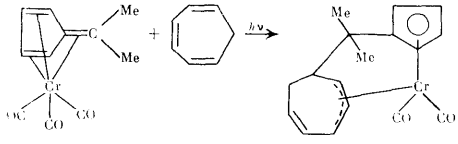
The protonation of complexes of 6-(*N*,*N*-dimethylamino)-fulvene with chromium, molybdenum, and tungsten carbonyls was studied in 1980 by ^{1}H NMR and infrared spectroscopy under the conditions of different acidities in solutions of trifluoroacetic and acetic acid in methylene chloride[45]. It was established that in CF_3COOH the complexes are reversibly protonated at the metal atom and that the rate of protonation varies linearly with the acidity of the medium:

$$(C_5H_4CHNMe_2)M(CO)_3 \underset{Et_2NH}{\overset{H^+}{\rightleftharpoons}} [(C_5H_4CHNMe_2)M(CO)_3H]^+ ;$$
$$M = Cr, Mo, W .$$

Signals are then observed in the ^{1}H NMR spectra in the range of δ values between −3 and −8 p.p.m., which are characteristic of hydrogen atoms linked to a metal. With increase of the atomic number of the metal, the signals are displaced to higher field, which indicates an increase of the degree of shielding of the hydrogen atom attached to the metal. The authors estimated quantitatively the relative basicities of the complexes of 6-(*N*,*N*-dimethylamino)fulvene with Group VIB metal carbonyls and found that the basicity of the complexes increases in proportions of ~1 : 150 : 1800 with increase of the atomic number of the metal from Cr to Mo and then to W.

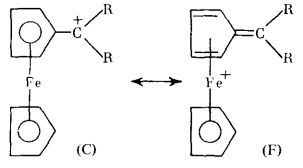
As already stated, previously the qualitative conclusion was reached that the basicity of the complexes of triphenylphosphonium cyclopentadienylide with Group VIB metal carbonyls increases with increase of the atomic number of the metal.

The reaction of 6,6-dimethylfulvenechromium tricarbonyl with cycloheptatriene in hexane under irradiation, which leads to the formation of a complex having a composite structure, has also been described[46]:



5. Metallocenylcarbenium Ions

The metallocenylcarbenium ions, which are readily formed and exhibit an unusual stability, can also be included in the class of pentafulvene complexes with transition metals:

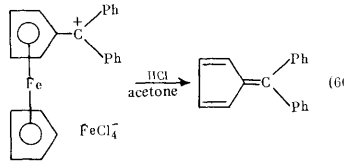


(C) (F)

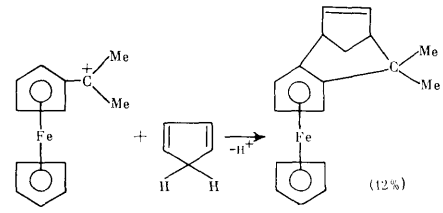
The authors of a review on fulvene complexes[3] regard α-ferrocenylcarbenium ions as complexes with a fulvene ligand. Although the nature of the unusually high stability of the α-ferrocenylcarbenium ions has been the subject of prolonged discussion and there have been many publications on this subject (original and review publications)[47–49], the structure of these species has still not been finally established.

Being unable to consider this question in detail, we shall confine ourselves only to listing the pieces of evidence characterising the interrelation between the fulvene (F) and ferrocenylcarbenium (C) structures and to a discussion of the results of a recent investigation[50] undertaken to determine the structure of the tetrafluoroborate of the diphenylferrocenylcarbenium ion.

One of the pieces of evidence in support of the fulvene structure of the ferrocenylcarbenium ion is the spontaneous formation of fulvenes from the latter in hydrochloric acid solution or under irradiation[51–54], for example:

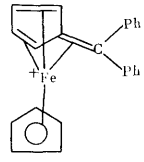


Another important piece of evidence is the ability of ferrocenylcarbenium ions to interact with cyclopentadiene to form a cycloaddition product[55]:



Quantum-chemical calculations on ferrocenylcarbenium ions have shown that a considerable proportion of the positive charge is located at the iron atom[56]. The study of the ^{1}H and ^{13}C NMR spectra (see, for example, Refs.57–59) has shown that the positive charge is distributed throughout the molecule of the complex.

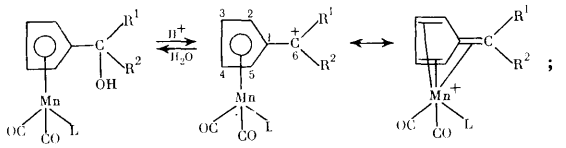
A complete X-ray diffraction analysis of the tetrafluoroborate of the diphenylferrocenylcarbenium ion has been carried out quite recently[50]. The experimental data enabled the author to conclude that the compound is a salt of the fulvene-cyclopentadienyliron cation:



In this system the exocyclic carbon atom is displaced from the plane of the cyclopentadienyl ring in the direction of the iron atom by 20.7°. The exocyclic carbon–carbon bond is appreciably shorter than the simple C–C bond and alternation of bond lengths is observed in the cyclopentadienyl ring, in a manner similar to that established previously for the isoelectronic diphenylfulvenechromium tricarbonyl[40,41]. Analysis of the results led the author[50] to the conclusion that the metallocenylcarbenium ion is stabilised not only as a result of the interaction of the orbital of the exocyclic carbon atom with the molecular orbital of the cyclopentadienyl ring but also as a consequence of the formation of a bond between this carbon atom and the central iron atom.

Like ferrocene, ruthenocene and osmocene greatly stabilise the neighbouring cationic centre[60,61] and therefore α-ruthenocenyl- and α-osmocenyl-carbenium ions can also be regarded as fulvene complexes.

The systematic study of cymantrenylcarbenium ions has been begun comparatively recently[62-69]. Like the ferrocenylcarbenium ions, these ions are formed when the corresponding carbinols are dissolved in acid. Solutions of the cations are extremely stable:



R^1, R^2 = Ph, C_6H_4Me, $C_6H_4CMe_3$, Me, Et etc.,
L = CO, PPh_3, $P(OPh)_3$, PEt_3, $SbPh_3$ etc.

The structure of the cymantrenylcarbenium ions is apparently analogous to that of the corresponding ferrocenyl ions. This is indicated, for example, by the study of the ^1H and ^{13}C NMR spectra, whose results indicate a pronounced delocalisation of the positive charge over the cymantrenyl fragment[65]. Diastereotopy of the protons in the 2- and 5-positions[68,69] similar to that observed earlier for ferrocenyl ions[70], has been observed for cymantrenylcarbenium ions[68,69]; it can be accounted for by the hindered rotation about the C(1)–C(6) bond, which has some double bond character. However, the lack of X-ray diffraction data for carbenium ions stabilised by cymantrenyl residues precludes a final conclusion concerning the full similarity of their structure with that of ferrocenylcarbenium ions.

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The extremely important and interesting available information about the influence of π-coordination to a transition metal atom on the properties of the cyclopentadienyl ring, carrying a full or partial negative charge, cannot as yet be regarded as sufficiently complete. It has been shown from the results of an X-ray diffraction study of dimethylsulphonium cyclopentadienylide (~80% contribution of the dipolar structure) and of its π-complex with the $Cr(CO)_3$ group that the π-coordination of this ylide is not accompanied by sharp changes in the structure of the cyclopentadienylide, but leads to an appreciable equalisation of the C–C bond lengths in the five-membered ring, i.e. to an increase of the contribution of the ylide structure in the π-ligand. In contrast to this, in the case of 6,6-diphenylfulvene, which has the ylene structure, π-coordination to the $Cr(CO)_3$ group leads to the breakdown of the planarity of the fulvene system owing to the deviation of the exocyclic carbon atom in the direction of the chromium atom. In this case the butadiene system of the five-membered ring and the exocyclic double bond are coordinated to the metal. As a result of the coordination of 6-(*N*,*N*-dimethylamino)fulvene (contribution of the dipolar structure ~50%) to the $Cr(CO)_3$ group, the molecule of the complex contains the fulvene ligand in its dipolar form.

The results of the study of the ^{13}C NMR spectra of the complexes of dimethylsulphonium and triphenylphosphonium cyclopentadienylides with Group VIB metal carbonyls showed that the differences between the chemical shifts of the carbon nuclei in the cyclopentadienyl ring diminish sharply on π-coordination to transition metals and an appreciable equalisation of the electron density in the five-membered ring occurs as a result. The observed ability of the π-complexes of cyclopentadienylides with Group VIB metal carbonyls to undergo hydrogen isotope exchange with deuteroethanol in neutral media made it possible to employ the hydrogen isotope exchange method to compare the reactivities of the ylide and their π-complexes.

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Polymerisation Filling by the Method of Radical Polymerisation as a Procedure for the Preparation of Composite Materials

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Studies devoted to the polymerisation of monomers in the presence of dispersed fillers are surveyed. Attention is concentrated on systems where polymerisation accompanied by the formation of a chemical bond between the polymer matrix and the filler takes place. Procedures for polymerisation filling and the preparation of filled polymer compositions are described systematically and analysed; the characteristics and general features of radical polymerisation initiated from the surface of the solid phase, usually from the surfaces of dispersed inorganic fillers, are discussed. Cases of improvement of the physicochemical and operational properties of compositions resulting from the formation of the chemical bond between the polymer matrix and the filler are examined.
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I. INTRODUCTION

In recent years filled polymer compositions have been finding increasing applications in various branches of technology[1,2]. The introduction of solid dispersed or fibrous inorganic or organic substances into the polymer phase makes it possible not only to reduce significantly the cost of polymeric materials by employing cheap and readily available fillers but also this frequently leads to the strengthening of the materials, i.e. to an improvement of their physicochemical, mechanical, thermal, electrical, friction, and other properties. There is then a possibility of replacing expensive constructional plastics (polyamides and polyesters) by cheaper filled polymers[3-5].

Cheap and readily available mineral fillers constitute an increasing proportion of the overall volume of fillers employed and their assortment is being continuously increased[2,6,7]. Thus it is believed that the employment of fillers for plastics will have increased from 1.06×10^6 tonnes in 1975 to 15×10^6 tonnes in 2000, including the following substances (in million tonnes): carbonates (mainly chalk) from 0.7 to 9.0, asbestos from 0.18 to 1.7, aluminium hydroxide from 0.05 to 1.6, talc from 0.04 to 1.8, cellulose from 0.4 to 0.5, silicates from 0.025 to 0.5, and glass from 0.1 to 0.2.

We may note that the criterion of cost-effectiveness of filled compositions is not their absolute cost (the composition can be more expensive than the matrix polymer). It is in fact the difference in cost relative to the material replaced. For this reason, the most expensive fillers, which also have the greatest reinforcing effect, for example carbon fibre, are sometimes used in compositions based on fairly cheap polymers[8,9].

The most important factor which determines the strengthening effects of fillers in polymers is the adhesion of the polymers to the surfaces of the fillers[1,10,11], which depends on the adsorption and chemical linkages between the surface of the filler and the polymer matrix. The interaction of the polymer with the surface of the filler determines the nature of the deformation and breakdown of the filled polymer and many other properties. It is noteworthy that in the general case organic polymers are as a rule poorly compatible with inorganic fillers.

One of the ways of improving adhesion may be the employment of a third component (dressing agent) which forms an intermediate layer between the polymer matrix and the filler[1]. This approach can be conveniently employed in the stage involving the processing of the polymer by dressing the filler before mixing it with the polymer. In many cases expensive dressing agents with a complex structure must be used to achieve the necessary effect[12,13]. The mixing equipment and technology, which are in many instances specific to a particular polymer–filler combination, must be chosen taking into account the abrasive effect of the filler, which frequently becomes the key factor in the solution of the problem of preparation of filled compositions[7].

The mechanism of the strengthening effect of fillers in filled compositions has not so far been completely elucidated[14-17]. A common idea is that the difference between the moduli of elasticity of the polymer matrix and the filler is the cause of the "concentration" of the breaking stress at the interface between the polymer mass and the filler particle[18,19]. This phenomenon can be eliminated if the filler particle has been encapsulated in a polymer phase bound closely to it and having a modulus of elasticity close to that of the filler. It is believed[18] that such a capsule may consist of a polymer matrix linked by covalent bonds to the filler particle.

Together with the improvement of the physicomechanical and operational properties of the composition on formation of a chemical bond between the polymer matrix and the filler, the possibility of improving the rheological characteristics of the melt of the composition and its capacity for being worked has been noted in a number of studies[20].

The commonest methods ensuring the formation of a chemical bond between the polymer matrix and the filler consist in the introduction of the filler into the polymer and at the stage involving its processing, using dressing agents or functional groups on the surface of the filler and the polymer matrix[1]. However, the method of polymerisation filling, a realistic version of which has been recently proposed and applied by Enikolopov[21,22], is of greatest interest. Its essential feature reduces to the polymerisation of the monomer in the presence of a dispersed filler with a catalytic system deposited on its surface. In this case it is easy to ensure the encapsulation of the filler in a polymer "jacket".

The advantage of polymerisation filling as a procedure for the preparation of compositions consists in the ease of measuring out the amounts of the components and the elimination from the technological scheme of a series of

operations associated with the dressing of the filler and the homogenisation of the components.

Fairly numerous literature data concerning various procedures for polymerisation filling by radical polymerisation have been published recently; a number of specific features of the polymerisation of vinyl monomers, accompanied by the formation of a polymer bound chemically to the surface of the filler, have been discovered. However, there has been no systematic account of these data so far. The review of Kroker et al.[23] partly reflects the essential feature of the problem, but the intense development of this field in recent years makes it necessary to supplement significantly and analyse these data.

The aim of the present communication is to give a systematic account and to analyse the methods for polymerisation filling and the preparation of filled polymer compositions described in the literature. The general characteristics of radical polymerisation initiated from the surface of a solid phase, usually from the surfaces of dispersed inorganic fillers, are discussed.

II. PROCEDURES FOR THE POLYMERISATION FILLING OF POLYMERS BY THE METHOD OF RADICAL POLYMERISATION

The earliest communications concerning the possibility of preparing polymers bound chemically to the surfaces of mineral fillers directly in the polymerisation stage are associated with the initiation of the process by mechanochemical reactions. This possibility arises when fillers subjected to grinding and cleavage with the aid of a wide variety of apparatus for the comminution of solids are employed. The active centres formed on the surface of the filler under these conditions can initiate polymerisation.

One of the first communications on this field[24] dealt with the polymerisation of styrene, α-methylstyrene, butadiene, and chloroprene on grinding with silica in a ball mill in an atmosphere of nitrogen; the amount of non-extractable polymer was ~0.2–2%. Polymers grafted onto the surface of the filler have been obtained[25] as a result of the polymerisation of a number of monomers in the milling of titanium dioxide. Grafted polymers have been obtained[26] on vibration of monomeric specimens filled with Group III or VIII metal oxides. Vibration of dried sodium bentonite in the presence of methyl methacrylate[27] leads to polymerisation and the formation of a polymer bound chemically to the filler (yield up to 22%); a homopolymer is not then formed. On the other hand, when benzoyl peroxide was added to the reaction mixture, homopolymerisation took place.

It is striking that in the above communications no direct evidence is presented for the presence of covalent bonds between the macromolecules and the solid surface nor are any ideas concerning the mechanisms of the processes involving mechanochemical reactions described. Nevertheless Kroker et al.[23] assumed that the radicals formed on the solid surface as a result of the homolytic cleavage of chemical bonds by mechanical influences are responsible for the initiation of polymerisation. However, it has been shown in a number of studies by Kargin and Plate[28–31] and by Tsetlin[32,33] that radical-ions are the active centres which are formed on the surfaces of the solid particles during their comminution and initiate polymerisation.

A systematic study of the mechanochemical graft polymerisation on a wide variety of solid surfaces of different monomers[34–37] enabled the authors to establish a series of common features, on the basis of which a mechanism of the grafting process has been proposed[38]. Grafting was achieved in the course of the dispersion of coarsely disperse powders (calcium carbonate, barium sulphate, ionic single crystals of NaCl, LiF, and CaF_2, magnesium oxide, iron oxide, graphite, amorphous glasses, quartz, metals, and polymers) in a vibromill in the presence of the monomer in air or on powders and cleaved single crystals obtained in air or in argon with subsequent contact between the specimen and the monomer (styrene and methyl methacrylate).

The authors[34–38] reached the following conclusions. The degree of grafting depends quantitatively on the nature of the surface, but grafting does not exhibit specificity and occurs on the surfaces of solids with a wide variety of structures and chemical bonds. The formation of the homopolymer together with the grafted polymer is not due to polymerisation but is a consequence of the stripping off and dissolution of part of the layer of the grafted macromolecules formed. A proportion of the homopolymer can be formed as a result of the radiation effect of electron emission[39] and the influence of the latter can be manifested only when the filler is dispersed directly in the presence of the monomer. The aftereffect in the initiation of polymerisation persists for a long time, exceeding by several orders of magnitude the electron emission time.

The main conclusion reached in the series of the above studies[34–39] is that the mechanochemical initiation of polymerisation takes place via a free-radical mechanism. The role of the centre stimulating the initiation of polymerisation can be assumed also by the free (static) charges arising on comminution of the solid and persisting on the freshly formed surface for a very long time after electron emission has stopped.

Certain additional ideas about the mechanism of graft polymerisation or the mechanochemical method of initiation can be derived from recently published studies[40–42]. In a study of the polymerisation of styrene on the freshly formed surfaces of NaCl, KCl, and LiF [40,42] and shale of different origin[41], the authors concluded that the polymer is grafted to the negatively charged centres of the crystals[40,42] and on the charged defects of the surface of shale[41].

It is seen from the foregoing that, despite the growing interest in the mechanochemical initiation of graft polymerisation, the problem of the mechanisms of initiation and the formation of the grafted polymer has not been ultimately elucidated.

The mechanochemical method of activating the surfaces of solid inorganic substances for the initiation of graft polymerisation is not unique. Thus extremely effective initiation of polymerisation by molecular beams of crystallised substances has been achieved[28]. The possibility of the polymerisation of methyl methacrylate and styrene using the surface energies of specimens comprising the oxides SiO_2, BeO, and Al_2O_3, having atomically clean dehydrated surfaces, has been established[43]. Such an "unsaturated" surface of a solid inorganic substance, free from extraneous adsorption layers, exhibits a considerable reactivity by virtue of the large excess of free energy, which is the reason for the ease of the chemisorption of the monomer and the subsequent initiation of its polymerisation by the active surface centres (ionic or radical).[29] The polymerisation was carried out in a layer of monomer deposited on the surface either from solution or from the vapour phase. It has been suggested[43] that the polymerisation of methyl methacrylate is accomplished by the grafting of the polymer to the surface, judging from the amount of the non-extractable polymer (80–90%). However, in contrast to poly(methyl methacrylate), the grafting of polystyrene was not observed. We therefore believe that the presence of the non-extractable poly(methyl methacrylate) is most probably associated with the chemisorption of the polymer on the surfaces of the

oxides with formation of carboxylate ions of the type $(R - C(=O)-O)^- Me^+$ and not the formation of polymer–filler covalent bonds. Infrared spectroscopic studies revealed[43] the chemisorption of methyl methacrylate on both hydrated and atomically clean Al_2O_3 surfaces.

An interesting method for the activation of the surfaces of mineral fillers in order to achieve polymerisation filling has been proposed by Berg et al.[44], who reported the ability of styrene and ethyl vinyl ether to polymerise on the surface of SiO_2 (in the form of Aerosil) activated with the aid of plasma. The yield of polymers is then higher when the activation is carried out in an oxygen and not an argon plasma. The average molecular weight of the products was 4×10^3 and the main bulk of the polymer formed was grafted to SiO_2.

One of the first productive methods for the preparation of polymers grafted to the surfaces of fillers is based on the use of irradiation. Thus the preparation of grafted polystyrene and poly(methyl methacrylate) on the surfaces of a wide variety of mineral fillers subjected to preliminary γ-irradiation has been reported[45,46]. According to Dinh-Ngoc et al.[45], γ-irradiated fillers have reaction centres capable of existing for up to 20 days and distributed exclusively on the surface. The amounts of grafted polymer per unit area are approximately of the same order of magnitude for different fillers (Table 1); the homopolymer is hardly formed under these conditions.

Table 1. The results of the polymerisation[45] of styrene and methyl methacrylate on a filler surface subjected to preliminary irradiation.

Monomer	Filler	Yield of grafted polymer			s
		w_1	w_2	$10^4 w_3$	
Methyl methacrylate	Silica gel	0.06	0.57	12.7	450
Methyl methacrylate	Woelm	0.03	0.40	8.9	—
Methyl methacrylate	Sikron	0.0008	0.0035	5.8	6
Methyl methacrylate	$CaCO_3$	0.003	0.009	14.5	1.5
Styrene	Silica gel	0.05	0.19	4.1	—
Styrene	Calcite	0.00	0.0045	7.3	—

Notation: w_1 and w_2 are the yields on a non-irradiated surface and in postpolymerisation (grammes per gramme of filler), w_3 is the yield in postpolymerisation (g m^{-2}), and s the specific surface (m^2 per gramme of filler).

Polymerisation in the presence of fillers initiated directly by γ-irradiation has been investigated in a number of studies[46–63]. The reaction takes place in a layer of monomer adsorbed from the gas phase on the surface of the specimen of the mineral filler (silica gel and Aerosil). It has been suggested that surface silanol groups are responsible in this instance for the grafting of the polymer[47–49]. The polymerisation of vinyl acetate and acrylonitrile on the surfaces of inorganic fillers has been interpreted[47,48] as an inhibited reaction occurring under conditions where the concentration of a relatively ineffective inhibitor—surface hydroxy-groups involved in degenerate chain transfer—is high. It is assumed that the surface radicals $\geqslant SiO^\cdot$ and $\geqslant Si^\cdot$—arise under the influence of irradiation, which can lead to the formation of grafted polymers[50].

In contrast to an earlier study[51], it has been noted[52] that the polymerisation of vinyl acetate and acrylonitrile adsorbed from the vapour phase on the surface of Aerosil results in the formation, already in the initial stage, of a considerable amount (50%) of a polymer which is not grafted to the surface and the authors believe that this is caused by the formation in the system, as a result of the radiolysis of silanol groups, of low-molecular-weight radical species $H^\cdot$ and $OH^\cdot$, which are not bound chemically to the solid support. Radicals arising in chain transfer to the monomer can play a definite role in the formation of the grafted polymer[48], whereas the role of the radicals formed as a result of the direct absorption of the radiation energy by the adsorbed monomer is apparently not great[47,48].

A considerable influence of adsorption–desorption processes on the formation of the polymer phase on a solid support in such systems has been noted[53]. The amount of styrene adsorbed on silica gel has been varied[54] from the value corresponding to less than a monolayer up to the level of uniform adsorption. It has been shown that the rate of graft polymerisation and the molecular weight distribution (MWD) (Fig. 1) of the polymer formed vary with the amount of adsorbed styrene; the maximum effectiveness of the grafting has bee achieved under the conditions of monolayer adsorption.

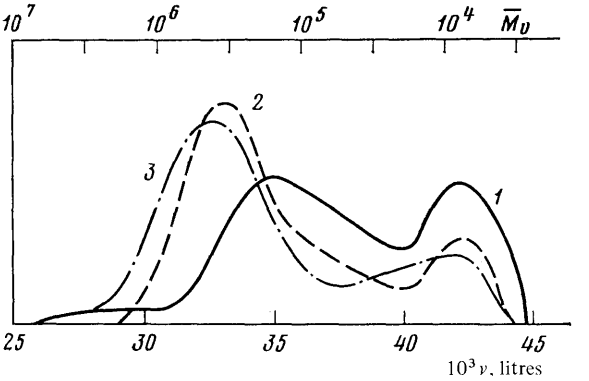


Figure 1. The molecular-weight distribution (MWD) of polystyrene grafted to silica gel and obtained in 1 h at a dose rate of 1×10^6 rad h^{-1} for different amounts of the monomer adsorbed on the filler; number of monolayers; *1*) 0.5; *2*) 1; *3*) 3 (v is the volume of eluent).[54]

A considerable change in the kinetic parameters of the polymerisation of vinyl acetate adsorbed on Aerosil relative to the liquid-phase polymerisation has been observed[55]: the rate constants for chain propagation and bimolecular termination decrease by 1–1.5 and 5 orders of magnitude respectively.

Believing that surface silanol groups are responsible for grafting, Japanese investigators[46,49,54,56–62] have adopted a different point of view concerning the mechanism of radiation-induced graft polymerisation. When the study of the polymerisation of styrene and methyl methacrylate in the presence of silica gel and Aerosil established that both grafted polymer and the homopolymer are formed simultaneously via both ionic and radical mechanisms over the entire range of dose rates. This conclusion is based on the analysis of GPC (gel permeation chromatography) peaks

which in the case of both the grafted polymer and homopolymers are bimodal, and also in the study of the influence of the dose rate and reaction temperature[57,60] and the presence of the inhibitors of radical and ionic reactions[61,62] on the nature of the GPC peaks. Analysis of the results of the polymerisation of styrene in the presence of various fillers (Aerosil and silica gel) led to the conclusion that the impurities and microporosity do not influence the reaction mechanism[59].

It has been noted in all the studies that the yield of the homopolymer always exceeds that of the grafted polymer but the molecular weight of the grafted polymer is higher (Fig.2) than that of the homopolymer. The grafted polymer, formed via a radical mechanism, has a higher molecular weight than the polymer formed via an ionic mechanism. It has been noted that in the presence of fillers (Aerosil, silica gel, and alumina) the rate of polymerisation is higher than in their absence. It has been suggested that this acceleration is associated with the excitation of the monomer molecules or of the growing chain by energy transfer from the filler[55,58].

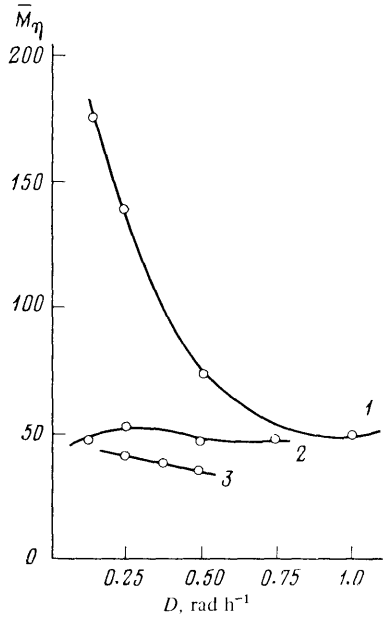


Figure 2. Dependence of M_η for polystyrene on the irradiation dose D: *1*) polystyrene grafted to silica gel; *2*) homopolymer; *3*) polymer obtained in the absence of the filler[56].

From a practical point of view, it is not without interest that on γ-irradiation a mixture of silica gel and styrene forms a greater amount of grafted polymer than in the grafting of styrene on silica gel subjected to preliminary irradiation[63].

The photochemical vapour-phase graft polymerisation of acrylonitrile, methyl methacrylate, and styrene on Aerosil with a peroxide coating, obtained using t-butyl hydroperoxide under conditions described by Poletukha[65], has been achieved[64]. Acrylonitrile has also been polymerised on Aerosil with a chlorosilylated coating[66] and on Aerosil with adsorbed quinones[67]. Analysis of infrared spectroscopic and gravimetric data led the authors of[64,66] to the conclusion that, when the modified silica is acted upon by ultraviolet light, the peroxide and chlorosilylated coatings decompose photochemically with formation of the corresponding radicals:

$$\equiv\!Si{-}O{-}O{-}C_4H_9 \xrightarrow{h\nu} \equiv\!Si{-}O^{\cdot} + C_4H_9O^{\cdot}\ ;$$

$$\equiv\!SiCl \xrightarrow{h\nu} \equiv\!Si^{\cdot} + Cl^{\cdot}\ .$$

It has been shown[68] that the quinone adsorbed on Aerosil is reduced by ultraviolet light as a result of the phototransfer of hydrogen atoms from the surface hydroxyls with formation of the radicals $\equiv$SiO$^{\cdot}$, which are also believed to be formed[68] in the photodehydration of the silanol groups of silica. The surface radicals $\equiv$SiO$^{\cdot}$ and Si$^{\cdot}$ initiate the graft polymerisation of monomers, particularly acrylonitrile:

$$\equiv\!Si{-}O^{\cdot} + n\,CH_2{=}CH \rightarrow \equiv\!Si{-}O{-}(-CH_2{-}\underset{CN}{CH}{-})_n{-}\ ,$$

$$\equiv\!Si^{\cdot} + n\,CH_2{=}CH \rightarrow \equiv\!Si{-}(-CH_2{-}\underset{CN}{CH}{-})_n{-}\ .$$

According to extraction data, the content of the homopolymer in the overall amount of polyacrylonitrile does not exceed 20%.[67]

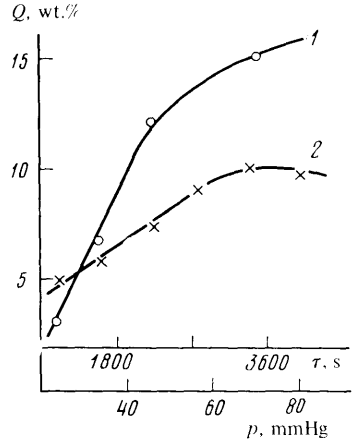


Figure 3. Dependence of the yield Q of the grafted polyacrylonitrile (at a monomer vapour pressure of 80 mmHg) on the time τ (curve *1*) and on the vapour pressure of the monomer p (curve *2*); irradiation for 45 min at 25 °C.[67]

The radical mechanism of the graft polymerisation of acrylonitrile on Aerosil is also indicated by the reaction order with respect to the intensity of the irradiating light (0.5) and by the inhibition of the reaction by oxygen[67,69]. The authors[67,69] investigated certain features of the mechanism of the photochemical vapour-phase graft polymerisation of acrylonitrile on Aerosil with quinone and peroxide coatings. It was established that, in contrast to the gas-phase radiation-chemical graft polymerisation, the yield of the polymer after prolonged ultraviolet light irradiation reaches a maximum value (Fig.3). This finding as well as data obtained in the study of the effect of the acrylonitrile vapour pressure on the rate of polymerisation (Fig.3) and the

observed[69] negative temperature coefficient of the reaction have shown that the rate of graft polymerisation of acrylonitrile on Aerosil is determined by the concentration of the monomer in the sorption layer and not in the vapour phase, i.e. the process proceeds via a sorption mechanism.

It is noteworthy that postpolymerisation is not observed in the system investigated, which shows that the radicals $\equiv SiO^{\cdot}$ are rapidly deactivated under the experimental conditions. The absence of an aftereffect served as a basis for the hypothesis[33] that the initiation of the radiation-chemical graft polymerisation, where postpolymerisation takes place, is due to other radicals, whose nature has not been established. It has been noted[69] that the Aerosil surface has no specific catalytic effect on the polymerisation taking place in the test systems, because the activation energy for the given process is close to the value for the photochemical polymerisation of acrylonitrile in bulk.

Table 2. The influence of the nature of the monomer, the inorganic compound, and the initiator on the yield of the grafted polymer[70].

No.	Filler	s, m^2 per gramme of filler	Initiator	Polymer	Yield of polymer		α, %
					m_1	m_2	
1	Al_2O_3	93.80	APS	PAN	20.0	13.0	69.0
2	Al_2O_3	93.80	BP	PAN	0	0	0
3	Al_2O_3	93.80	APS	PAA	55.4	53.6	97.0
4	Al_2O_3	93.80	BP	PAA	10.7	8.0	73.0
5	Al_2O_3	93.80	APS	PMAA	30.0	26.4	87.6
6	Al_2O_3	119.00	APS	PAN	26.3	17.9	72.2
7	Al_2O_3	145.00	APS	PAN	43.4	38.4	88.5
8	$CaCO_3$	0.12	APS	PMAA	15.6	15.1	97.0
9	$CaCO_3$	0.12	APS	PAA	33.6	33.5	99.0
10	TiO_2	3.50	APS	PAN	22.8	3.5	15.4
11	TiO_2	3.50	APS	PMMA	12.4	1.0	8.8
12	ZnO	2.40	APS	PMMA	9.6	0.8	8.1
13	Al	0.12	APS	PAA	8.3	3.7	44.2
14	Al	0.12	BP	PMMA	27.0	2.7	10.0
15	Al	0.12	BP	PVA	12.8	2.9	22.3

Notation: APS = ammonium persulphate; BP = benzoyl peroxide; PAN = polyacrylonitrile; PAA = poly(acrylic acid); PMAA = poly(methacrylic acid); PMMA = poly(methyl methacrylate); PVA = poly(vinyl acetate); m_1 and m_2 = amount of polymer formed and the amount of polymer after extraction (% of weight of substrate); α = fraction of grafted polymer in the overall yield of polymer.

The graft polymerisation of a series of monomers has been achieved[70] under the influence of initiators preadsorbed on the surfaces of mineral fillers (Al_2O_3, TiO_2, $CaCO_3$, and Al). The polymerisation was carried out in a layer of monomer deposited from the liquid phase onto the surface of the filler. It has been observed (Table 2) that the effectiveness of the grafting depends to a large extent on the nature of the substrate, its specific surface, and the nature of the modifying polymer and the polymerisation initiator. When an initiator (benzoyl peroxide) soluble in monomers was used, the effectiveness of grafting was lower in all the experiments. Other conditions being equal, the effectiveness of grafting is higher for polymers insoluble in their own monomers (Table 2, Nos.1, 3, 5, and 10). It is believed[70] that this can be associated with the fact that, in the case of a monomer dissolving its own polymer (methyl methacrylate), the possibility of chain transfer via the monomer is greater. In many instances an extremum has been observed in the relation between the degree of conversion of the monomer and the amount of initiator (Fig.4) due to the fact that the initiator participates in the reaction not only in the initiation stage but also in the chain termination occurring both on the growing macroradicals and on the primary radicals. It has been suggested[70] that the graft polymerisation proceeds in this instance via a mechanism involving chain transfer from the initiator radicals, which has been examined in detail[71].

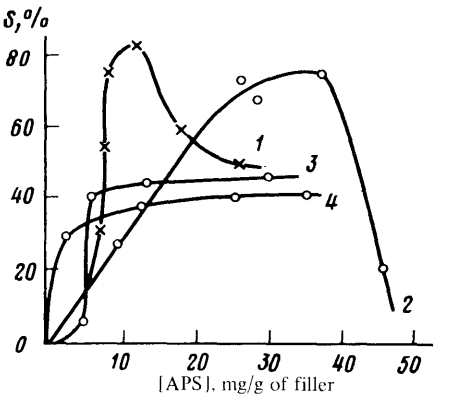


Figure 4. Dependence of the degree of conversion S of the monomer on the concentration of the ammonium persulphate (APS) initiator for the systems TiO_2–PAN (curve *1*), Al_2O_3–PMAA (curve *2*), Al_2O_3–PMAA (curve *3*), and Al_2O_3–PAM[PAN?] (curve *4*) at 60 °C (curves *1*, *2*, and *4*) and 70° (curve *3*) and for reaction times of 2.5 h (curve *1*), 4 h (curve *2*), and 5 h (curves *3* and *4*).[70]

Table 3. The content of polyacrylonitrile on the surfaces of mineral specimens[73].

Filler	g	Yield of polymer	
		m_1	m_2
Natural Sarigyukhsk bentonite	—	150	—
Sarigyukhsk bentonite in Na-form	0.32	200	144
Natural glauconite	—	3	—
Glauconite in Na-form	0.07	8.2	—
Glauconite in Na-form	0.09	11.2	7.5
Argillaceous-hydroxide adsorbent from Obolsk clay	—	31	—
Alkali-acid activated Al	0.11	28	23
Natural kaolin	0	0	—
Kaolin in Na-form	traces	1.6	1.2
KSK-2 *silica gel in* Na-form	0.02	1.2	0.7
Industrial KSK-2 silica gel	0	0	—

Notation: m_1 and m_2 = amount of polymer formed and amount of polymer after extraction (% of weight of filler); g = amount of Fe^{2+} absorbed by the filler (mequiv.g^{-1}).

A simple method has been proposed[72–74] for the preparation of grafted polymers on transition metal ion-modified (via an ion-exchange reaction) aluminosilicates and silica gel, which serve as components of oxidation-reduction systems initiating polymerisation in solutions and emulsions. In particular, it has been shown that acrylonitrile vinyl acetate, 4-vinylpyridine and acrylamide polymerise on the surfaces of a

series of $Fe^{2\pm}$ and $Cr^{3\pm}$ containing aluminosilicates in the presence of peroxy-compounds, part of the polymers being grafted to the solid surface (Table 3).

Graft polymerisation on chemically unmodified fillers in the presence of initiators has been described in a communication[75] dealing with a study where grafted copolymers used as pigments were obtained by dispersing a carbonaceous material (soot, coke, or graphite) in an aqueous medium together with the vinyl monomer (vinyl halides, styrene derivatives, unsaturated carboxylic acids, and dienes) in the presence of an oxidation-reduction initiating system.

It has been reported[76] that carbon fibres subjected to an oxidising treatment are capable of undergoing copolymerisation with methyl, ethyl, and n-butyl acrylates initiated by benzoyl peroxides. The rate of graft copolymerisation increases with increase of the degree of oxidation of the surfaces of the fibres and their monomer concentration.

An interesting method of initiating the graft polymerisation of vinyl monomers on the surface of glass has been described[77,78]. Reactive trichlorosilyl and trichloromethyl groups, which initiate the graft polymerisation of vinyl monomers in the presence of $Ni(CO)_6$ and $Mo(CO)_6$ respectively, were introduced onto the surface of glass beads by modifying the surface hydroxy-groups. The grafted polymer chains on the surface of the glass usually form a uniform monomolecular layer.

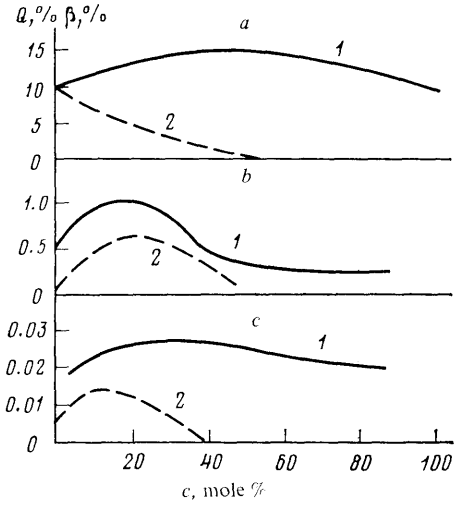
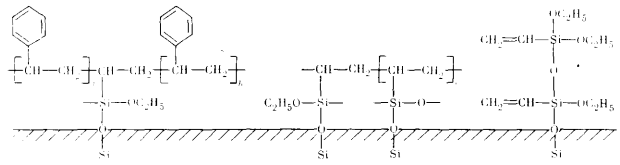


Figure 5. The influence of the composition of the monomer mixture on the yield Q of the grafted polymer (curve *1*) and the content of styrene units β in the grafted polymer (curve *2*): *a*) silica gel; *b*) broken brick; *c*) glass beads[79] (*c* is the content of triethoxyvinylsilane in the monomer mixture).

The polymerisation of binary monomeric triethoxyvinylsilane–styrene and triethoxyvinylsilane–methyl methacrylate systems on silica gel, quartz, glass beads, and brick dust has been investigated[79] with the reaction initiated by benzoyl peroxide or γ-radiation. In order to solve the problem of the sequence in which the copolymerisation and surface grafting reactions occur, a study was made of the influence of the composition of the monomer mixture on the yield of the grafted polymer, the content of the styrene and methyl methacrylate units in the grafted polymer, and the composition of the polymer. It was established (Fig.5), that, whereas the total amount of the grafted polymer does not depend greatly on the composition of the monomer mixture, the content of styrene and methyl methacrylate units in it is a maximum only in the mixture enriched in the corresponding monomer. The content of triethoxyvinylsilane in the grafted polymer is in all cases higher than in the monomer mixture.

On the grounds that the copolymerisation constants calculated from these data, namely r_1 (styrene) = 0.06 and r_2 (triethoxyvinylsilane) = 4.2, differ significantly from the literature values r_1 = 26 and r_2 = 0 (the corresponding values for methyl methacrylate are respectively r_1 = 37 and r_2 = 0), a conclusion has been reached[79] concerning the mechanism of the formation of the grafted copolymers. In the first place triethoxyvinylsilane condenses with the surface silanol groups and part of the triethoxyvinylsilane can polymerise with the partial opening of the double bond and another part gives rise to grafted polyethoxyvinylsilane as a result of the polycondensation of the ethoxy-groups. Next, some of the grafted triethoxyvinylsilane molecules undergo vinyl copolymerisation with the monomer under the influence of benzoyl peroxide or γ-radiation. It is of interest that the authors[79] were unable to separate the grafted polymer from the filler by dissolving the latter in hydrofluoric acid. They believe that this is due to the fact that the grafted copolymer closely shields the surface of the filler and hinders the access of HF to the latter.



Methacryloylmethyltriethoxyvinylsilane mixed with a monomeric dye has been polymerised[80] after impregnating fibres with the mixture (to achieve a more stable colour and more hydrophobic properties of the fibres. Conditions ensuring the quantitative grafting of the polymer have been determined. However, the quoted yield of the grafted polymer is apparently too high; this can be postulated bearing in mind the extremely low solubility of copolymers containing methacryloylmethyltriethoxysilane units[81] and their branching as a result of chain transfer to the methyl group of methacryloylmethyltriethoxysilane[82] and hence the difficulty of the separation of the grafted and ungrafted copolymers by the extraction method.

When 2,3-epoxypropyl methacrylate is polymerised on contact with a large area of a glass surface[83], the epoxy-groups are cleaved quantitatively, which leads to the formation of at least three different products. One of these, 2,3-dihydroxypropyl methacrylate, forms a polymer chemically bound to the glass in the course of the polymerisation process.

The possibility of obtaining graft polymers in polymerisation in the presence of inorganic fillers with the process initiated by free-radical initiators containing functional groups (carboxy-groups, etc.) has been described[84,85]. It is suggested that the functional groups of the initiator ensure the grafting of the polymer to the surface of the filler in the reaction with the surface silanol groups.

Organic peroxides have been used as initiators of this kind: t-butylperoxymaleic acid, peroxysuccinic acid, and their salts as well as a series of common organic and

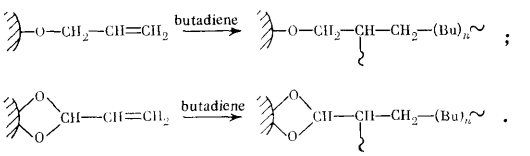
inorganic peroxides in combination with a reductant containing a carboxy-group, in the free state and in the form of the salt (malonic, oxalic, L-ascorbic, thioglycolic, and other acids and their salts). In order to obtain the maximum yield of the grafted polymer, the peroxide was added in an amount corresponding to 0.1–2.0 parts by weight to 100 parts by weight of the dispersion in water, ketones, ethers, and alcohols, while the reductant was added in an amount corresponding to 0.2–2.0 parts by weight for one part by weight of the peroxide. A wide variety of inorganic and organic solids in the form of a powder, fibre, film, sheets, etc. have been used as supports: metals and their oxides, sulphur, nitrogen, carbon, silicon, boron and chlorine compounds, the salts of various acids, hydroxides, and inorganic pigments.

It has been noted[84,85] that coating of the support with a mixture of grafted and ungrafted polymer in an amount corresponding to 3–50 parts per weight, about half of which corresponds to the polymer bound chemically to the filler, is in most cases the optimum procedure from the standpoint of the uniform coverage of the filler particles by the polymer and a satisfactory capacity of the product for being worked by pressing, extrusion, and casting under pressure. The specimens have a high bending strength. Thus a specimen made up of compressed filings coated with the product of the polymerisation of a mixture of ethyl acrylate, methyl methacrylate, and *N*-(hydroxymethyl)acrylamide in an aqueous suspension in the presence of benzoyl peroxide and oxalic acid had a bending strength of 840 kg cm^{-2}.

A procedure[85] for a uniform stable encapsulation of the filler in a polymer jacket which is bound chemically to it is noteworthy; the reaction is performed in a liquid medium containing the filler, the vinyl monomer, and the polymerisation initiator under conditions such that at least one reactant, giving rise to radicals, contains in its molecule a substituted or unsubstituted amino-group. Such a reactant can be both the monomer (mainly amino-derivatives of acrylates and methyl and ethyl methacrylates or monomers with nitrogen-containing heterocycles) and the initiator, for example the salt 2,2-azobis(2-amidinopropane) hydrochloride, as well as the peroxide–amine redox system usually employed as the radical polymerisation initiator. In most cases a high yield of the grafted polymer has been noted (80–90%). The composition produced has a high ultimate bending strength. Thus the ultimate bending strength of the specimen obtained by pressing grass charcoal coated with poly(methyl methacrylate) in an amount of 0.09 g per gram of filler was 383 kg cm^{-2}.

Publications concerning the polymerisation of monomers on the surfaces of fillers with grafted groups capable of polymerisation have appeared only recently. A method of binding the polymer to a silicon-containing support has been described[86]. The silicon-containing material in the form of individual particles is treated initially with an inorganic acid to increase the content of OH groups on its surface and then with an unsaturated silane (alkenyltrialkoxysilane or alkenyltrichlorosilane), after which the product is copolymerised with an unsaturated monomer having the general formula RCH = CHR', where R and R' = H, C_1–C_{10} alkyl or alkenyl, phenyl, amide group, or trichlorosilyl. These products are subjected to an additional treatment in order to introduce ion-exchange or chelate groups and are used to fill chromatographic columns.

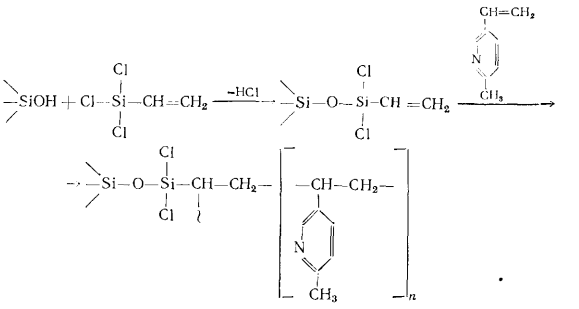
It has been shown[87,88] that unsaturated ethers and acetals, formed on interaction of the silanol groups of silica gel with allyl alcohol or acrolein respectively, copolymerise with butadiene in the presence of benzoyl peroxide:



The degree of conversion of butadiene is between 10 and 100%. An increased initial rate of polymerisation was noted when silica gel with unsaturated surface acetal groups was used. It is suggested that this finding is associated with the formation of additional radical centres owing to the thermal abstraction of hydrogen atoms from the allylic carbon atoms of the acetal group. The same workers[89] modified a silica filler with acrylonitrile and *N*-vinylpyridine. The use of such modified silica for copolymerisation with butadiene leads to an increase of the moduli of rupture and the resistance of the compositions to rupture.

The polymerisation of various monomers of the vinyl series, adsorbed from the gas phase on the surface of silica gel containing vinyl groups, has been investigated[90]. The reaction was initiated by adsorbed azobisisobutyronitrile at 60 °C. Up to 40 wt.% of the polymer bound chemically to silica gel is formed together with the homopolymer. It was found that the reaction order with respect to the initiator is 0.47, while that with respect to the monomer varies from 1 to 2.3. The reaction is of first order with respect to the monomer in polymolecular adsorption of the monomer, while higher reaction orders are obtained for degrees of adsorption corresponding to less than the monolayer coverage. The experimental data can be accounted for in terms of a kinetic reaction mechanism including as one of the elementary stages the grafting of the polymer to the surface by chain transfer and chain termination reactions on the free sections of silica gel with participation of both vinyl and silanol groups. The authors[90] believe that, as a consequence of the low concentration of the monomer in the gas phase and also the short lifetime of the surface radicals, the grafting of the polymer to the filler via the direct reaction of the monomer with the macromolecules growing on the surface is unlikely. The authors believe that the involvement in the copolymerisation of the vinyl groups grafted to the surface is insignificant by virtue of their low concentration on the surface and reduced reactivity caused by the resonance stabilisation due to the silicon atom.

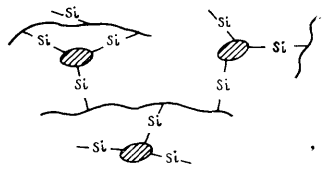
New mineral absorbents have been obtained[91] by the chemical grafting of certain monomers (vinylpyridines and *N*-vinylpyrrolidinone). For this purpose, a study was made of the graft copolymerisation of 2-methyl-5-vinylpyridine on vinyl-silica gel (silica gel with vinyl groups deposited on its surface by treatment with trichlorovinylsilane):



The process was carried out in the temperature range 70–80 °C and the initiator (diniz) and monomer concentrations were varied from 0.015 to 0.045 *N* and from 0.3 to 1.5 *N*

respectively. It was established that the yield of the grafted polymer increases with temperature, the initiator and monomer concentrations, and the amount of trichlorovinylsilane taken for surface treatment, but does not exceed ~12%. The kinetic features of the copolymerisation of monomers with a vinyl-substituted surface were discovered for the first time in systems of this kind. The reaction rate constants at 60°, 70°, and 80 °C are respectively 0.034, 0.128, and 0.376 litre$^{1/2}$ mol$^{-1/2}$ h^{-1}; the process activation energy is 25.9 kcal mol^{-1}. With the aid of computer search programmes, the authors[91] showed that the kinetics of the copolymerisation process can be described with the aid of the equation for ideal radical polymerisation.

Clay has been used in polymerisation filling[92]. After its treatment with (γ-methacryloyloxypropyl)trimethoxysilane followed by copolymerisation with styrene at 80 °C in the presence of azobisisobutyronitrile, the yield of the grafted polymer was 4.1–8.4% of the weight of the composition. The polymer consists of a gel which swells in benzene. Since the analogous copolymer obtained without a filler is soluble in benzene, it has been suggested that cross-linking via the following scheme takes place in the course of the graft copolymerisation:

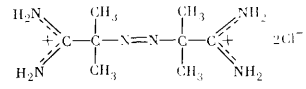


It has been noted that the analogous finished copolymer reacts less effectively with clay and does not form a gel, which has been explained by the reduced reactivity of the methoxysilane groups in the copolymer. These results agree with the features noted[79] in the copolymerisation of a binary monomer mixture in the presence of a filler where the active monomer is first attached to the surface and then the surface copolymerised with the second monomer.

The use of methacryloyloxymethyltriethoxysilane for the modification of Aerosil[93] makes it possible to obtain polymer compositions in which a considerable proportion (up to 23%) of poly(butyl methacrylate) is bound chemically to the surface of the filler. This results in a significant increase (by a factor greater than 4) of the tensile strength of the film based on the composition obtained relative to the composition based on unmodified Aerosil. It was established that the influence of the filler surface on the polymerisation kinetics is observed only when there is a possibility of the physical or chemical interaction of the monomer with the solid surface. The presence of the free comonomer of methacryloyloxymethyltriethoxysilane comonomer in an amount equal to that introduced together with the modified Aerosil did not affect the rate of the process.

The physicochemical and thermomechanical properties of certain polymerisation-filled systems have been investigated[94]. It has been noted that, as a result of the cross-linking of the poly(methyl methacrylate) macromolecules in the polymerisation of the monomer on allyl-substituted silica, the polymer becomes more rigid, which is reflected in its thermomechanical properties. The glass point of such a filled polymer is higher than that of the pure polymer by 12° and 19° respectively in the presence of 2.5 and 5 wt.% of allylsilica.

One of the new trends in the chemical modification of fillers is activation of the filler surface by initiating systems with subsequent polymerisation of the monomers on such a filler, serving as a carrier of active centres, and the formation of a chemically bound polymer. In this connection one should note studies[95,96] on the attachment of 2,2-azobisisobutyramidine hydrochloride to the surface of the filler (kaolin and bentonite) via an ion-exchange reaction and the initiation of the emulsion polymerisation of vinyl monomers by such systems.



(I)

According to Dekking's results[95], the attachment of the initiator to the surface entails an increase of the rate constant for its decomposition; the values of $10^4 k_{decomp}$ (s^{-1}) for compound (I) in a free form and attached to the filler surface are given below:

t, °C	(I)	(I)-kaolin	(I)-bentonite
60	0.358	0.666	—
70	1.41	2.17	3.33
80	5.01	9.91	10.13

The enthalpy and entropy of activation for the decomposition of the immobilised initiator have been determined (32.048 kcal mol^{-1} and +18.16 e.u. for kaolin and 30.227 kcal mol^{-1} and +13.20 e.u. for bentonite), their values being almost independent of the immobilisation of the initiator on the surface.

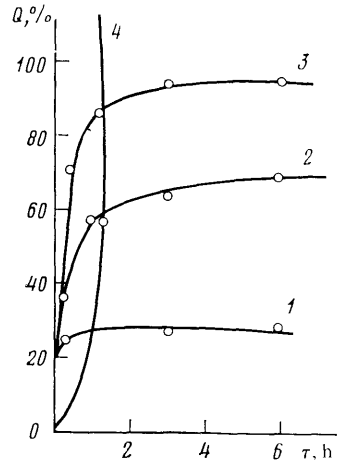
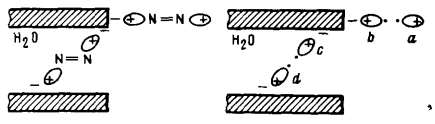


Figure 6. The yield of polymers Q in the emulsion polymerisation of methyl methacrylate initiated by the initiator–bentonite system (curves *1*–*3*) and by the initiator (curve *4*): *1*) grafted polymer; *2*) homopolymer; *3*) and *4*) overall yield of polymers[95].

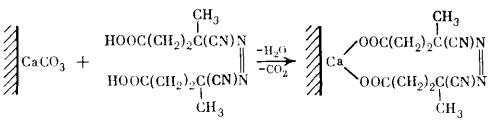
On immobilisation, the molecules of the initiator can behave in an ion-exchange reaction as monofunctional compounds, when they are located on the outer surface of the filler plates, and as bifunctional compounds when they are located between the plates and form monolayers of dications:



Determination of the ion-exchange capacity showed that in the case of bentonite ~80% of the initiator molecules are present on the surface in the form of dications and ~20% in the form of monocations. Radicals of types *b*, *c*, and *d* lead to the formation of polymers grafted to the filler, while radicals of type *a* lead to the homopolymer.

It was observed that the rate of formation of the homopolymer in the emulsion polymerisation of methyl methacrylate is approximatley twice as high as that of the grafted polymer (Fig.6), which can be explained by the difficulty with which the monomer approaches radicals of types *c* and *d*. The rate of formation of the homopolymer by a radical of type *a* is then six times higher than the rate of homopolymerisation of methyl methacrylate under analogous conditions but in the absence of the filler; the author[96] finds it difficult to account for this finding.

The influence of the grafting of the initiator to the particles of the solid filler on the rate of its thermal decomposition and its initiating activity in the polymerisation of vinyl monomers has been examined in a recently published communication[97]. The initiator was 4-azobis-4-cyanopentanoic acid (ACA) and the filler was calcium carbonate (chalk), their interaction resulting in the chemical grafting of the initiator to the surface of the chalk particles:



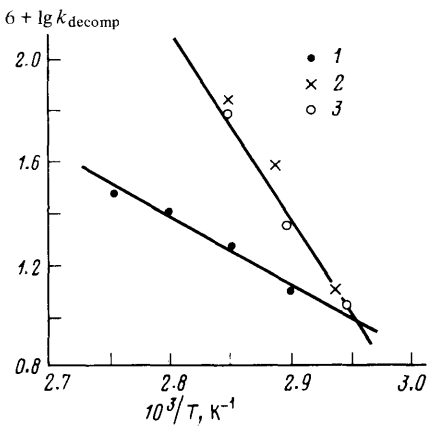
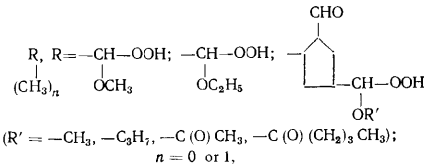


Figure 7. Temperature dependence of k_{decomp} for grafted ACA (curve *1*), ACA (curve *2*), and the calcium salt of ACA (curve *3*).[97]

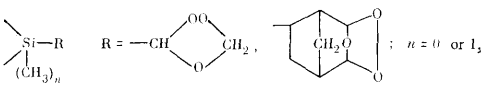
It has been established that the kinetic parameters of the thermal decomposition of the initiator change significantly in the chemical grafting of initiators to the surfaces of fillers. Thus the grafting of ACA to the solid phase lowers $k^{80°}_{decomp}$ (from 6.8×10^{-5} to 2.1×10^{-5} s^{-1}) and E^{a}_{decomp} (from 123.9 to 53.1 kJ mol^{-1}) (Fig.7). A sharp decrease of the rate of polymerisation of methyl methacrylate has been noted in the case where the initiator was grafted to the surface of the solid phase. The authors[97] explained these effects by the limited diffusional mobility of the radicals linked to the solid phase, which leads to the rapid recombination of the primary radicals, and also by topochemical factors due to the localisation of the initiation, propagation, and termination reactions at the surface of the particles. It has been shown that 3% conversion of methyl methacrylate into the polymer is sufficient to cover the entire surface of the chalk with a polymer "coating".

A simple method has been proposed recently[98] for the preparation of peroxidised mineral fillers, containing peroxy-groups with the general formula



which are capable of initiating polymerisation.

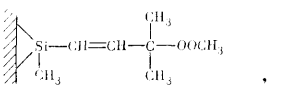
The method consists in the ozonisation of the mineral filler containing the grafted vinylmethylvinyl or norbornenylsilyl groups at temperatures between −20° and +20 °C in alcohol or in organic acid. When the ozonisation process is carried out in a hydrocarbon or its halogeno-derivative[99] at temperatures between −40° and +20 °C, peroxidised fillers with grafted ozonide peroxy-groups having the general formula



are obtained.

It has been shown[100] that the compounds produced when the temperature is raised may serve as a source of radicals bound to the filler, incapable of initiating the polymerisation of vinyl monomers, and giving rise to grafted polymers.

The same workers[101] investigated the characteristics of the polymerisation of styrene on the Aerosil A-175 filler with grafted dialkylperoxy-groups having the structure



The method of preparation of such fillers has been described[102].

An increased order of the reaction with respect to the monomer (1.68) was observed. The order of the reaction with respect to the initiator depends on the surface concentration of the latter and varies from 0.48 to 0.65 with increase of the density of the peroxy-groups on the surface of Aerosil (the concentration of active oxygen in the filler varies from 0.35 to 0.75 wt.%). The polystyrene formed consists of a polymer both grafted to the surface of Aerosil and the ungrafted homopolymer extractable with hot benzene. It has been established that the fraction of the polymer grafted to the surface of the filler depends on the polymerisation conditions and increases with increase of the temperature of the reaction, its duration, and the concentration of the peroxy-groups on the surface of Aerosil (Table 4 and Fig.8). When the monomer concentration is raised from 1.14 to 6.90 M, the yield of the grafted polymer increases from 0.38 to 2.75 g per gramme of Aerosil. The ratio of the amount of grafted polymer to that of the homopolymer increases with increasing surface concentration of peroxy-groups (Table 4) and the degree of conversation (Fig.8). It has been shown that k_{decomp} and E^{a}_{decomp} for the peroxide are independent of its concentration on the surface.

III. CHARACTERISTICS OF POLYMERISATION INITIATED FROM THE SURFACE OF A SOLID PHASE

The above analysis of the comparatively few studies on polymerisation filling, which have not always been combined in a single approach, indicates an endeavour to develop a method of preparation of composite materials which would permit the polymerisation of monomers (in bulk, in solution, or in an emulsion) in the presence of fillers with subsequent isolation of the finished composition using the familiar methods for the extraction of polymers from the reaction medium.

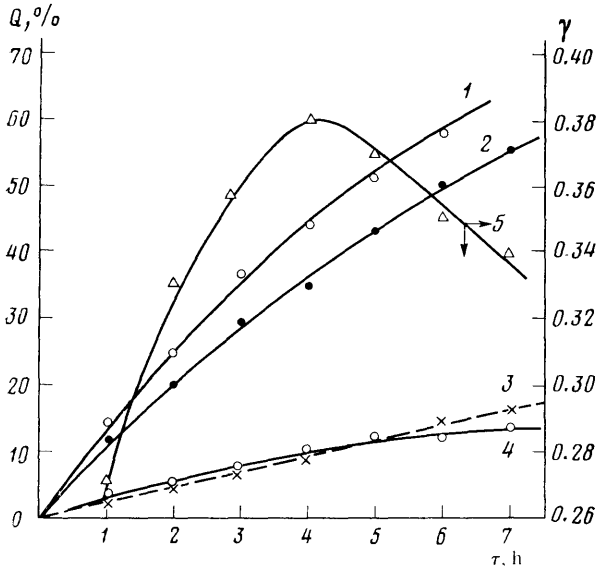


Figure 8. Dependence of the yield Q of polystyrene on the polymerisation time: *1*) overall product; *2*) homopolymer with allowance for the thermopolymer; *3*) thermopolymer; *4*) grafted polymer; *5*) ratio of the amounts of the grafted polymer and homopolymer γ (in the absence of thermopolymer); [M] = 2.02 M; [I] = 8.8×10^{-3} M; concentration of active oxygen on the filler surface 0.62 wt.%; 120 °C.[101]

The bond between the polymer and the surface of the filler arises directly during polymerisation and is due either to the effect of physical factors on the surface of the filler (γ- or ultraviolet irradiation, comminution and cleavage, or an increased temperature), inducing the formation of radicals which initiate the grafting of the polymer formed, or the copolymerisation of the vinyl monomers with monomers containing functional groups capable of chemical interaction with the surface functional groups of the filler (in the course of the copolymerisation or after its completion). Finally, there is a possibility of a third variant, where the polymerisation filling is achieved using fillers subjected to a preliminary modification by the grafting to the surfaces of polyfunctional monomers capable of copolymerisation or polyfunctional initiators capable of forming free radicals under the conditions of the polymerisation reaction.

There is no doubt that each method is distinguished by its specific features both from the standpoint of kinetic deviations from ideal radical polymerisation and from the standpoint of optimum yields of the grafted polymer, its characteristics, and the possibilities for the practical application of the methods. Unfortunately the amount of data concerning the amount of polymeric products bound to the surfaces of fillers and also information about the relative amounts of the grafted polymer and the homopolymer, the molecular weight characteristics of the polymers, and the properties of the compositions obtained are frequently insufficient for the analysis of the advantages of a particular method of polymerisation filling described in the literature quoted. Furthermore, in many instances there is no complete certainty that the solvent has been chosen correctly for the elimination of the homopolymer adsorbed on the surface. In this respect mention should be made of a study[52] where it was shown in relation to poly(vinyl acetate) that the probability of the dissolution of the polymer chain on the surface depends not only on the "quality" of the solvent in relation to the given polymer but also on the energy of the interaction of the solvent with the adsorption centres on the surface. In other words a "good" solvent in relation to the given polymer may prove to be a "poor" displacing agent and the polymer will not dissolve in it, which leads to unduly high results in the determination of the yield of the grafted polymer.

Table 4. Dependence of the rate of polymerisation of styrene ν and the yield of graft polymer Q on the conditions in the reaction initiated by a dialkyl peroxide grafted to the surface of Aerosil {chlorobenzene, [M] = 2.02 M [101]}.

t, °C	10^3[I], M	$10^5\nu$, mol litre^{-1} s^{-1}	Q, g/g of aerosil	γ, %
		c_{O_2} = 0.35 wt.%		
120	11.4	8.65	0.28	20.5
120	7.4	7.07	0.63	20.1
120	4.9	5.96	0.51	19.9
120	2.4	5.98	—	—
		c_{O_2} = 0.62 wt.%		
100	17.5	2.24	0.20	24.4
100	13.1	1.75	0.20	26.4
100	8.8	1.32	0.23	18.5
110	17.5	4.95	0.25	20.1
110	13.1	3.98	0.45	29.2
110	10.1	3.34	0.40	22.8
120	17.5	17.23	0.42	24.7
120	13.1	12.40	0.55	30.1
120	8.8	9.17	0.56	25.1
120	4.4	7.07	0.54	11.7
120	0.9	3.78	—	—
		c_{O_2} = 0.75 wt.%		
120	21.2	12.17	0.80	49.2
120	15.9	10.66	0.95	33.6
120	10.6	9.90	0.78	25.7
120	5.3	8.74	—	—
120*	10.6	9.60	—	—

Notation: c_{O_2} = content of active oxygen in Aerosil with grafted peroxy-groups; [I] = initiator concentration.

*In ethylbenzene.

Nevertheless, it is seen from the data presented that many characteristics of the graft polymerisation initiated by γ-irradiation (effective polymerisation only in a thin adsorption layer, influence of adsorption-desorption

processes on the formation of the graft polymer, and complexity of apparatus) are responsible for the limited applications of the given method. Mechanochemical initiation of graft polymerisation, which is frequently simple from the technological standpoint, does not ensure the attainment of the maximum possible coverages of the surface of the filler by the polymer layer, because the polymer is not grafted in a continuous coating but in the form of isolated spherical drops[103]. Photochemical initiation eliminates the disadvantages of other methods of polymerisation filling such as the formation of appreciable amounts of homopolymers and the degradation of the grafted layer. However, this method is not free from disadvantages characteristic of the method of initiation of graft polymerisation by γ-irradiation.

The method of the oxidation-reduction initiation of graft polymerisation is superior to the other procedures by virtue of its simplicity. Since many inorganic substances have ion-exchange properties and can be modified by transition metal ions, this method is fairly promising. The method of synthesising a surface-grafted polymer by the copolymerisation of monomers with a surface containing unsaturated bonds is one of the simple and effective methods of obtaining polymerisation-filled polymers.

The procedure based on the simultaneous polymerisation and grafting via the functional groups of the monomer is promising; this method eliminates the stage involving the preliminary treatment of the filler although it does not ensure the regulation of the density of the growth centres for macromolecules on the surface and is associated with an excess consumption of the active monomer and the formation of the copolymer not linked to the surface. The method based on the initiation of the reaction by agents capable of reacting with the surface via the functional groups of the initiator in the course of polymerisation is not free from these disadvantages either.

The method of polymerisation filling of polymers by filler-initiators is one of the interesting and new procedures for the preparation of composite materials, because it makes it possible to regulate fairly flexibly the process kinetics and the properties of the monomer layer bound to the filler particle by varying the density of the peroxy-groups on the surface and the polymerisation conditions; the stage in which a measured amount of the initiator is introduced is then significantly facilitated. The methods of synthesis of such fillers which have been described are suitable for technological application and the initiators themselves are universal for the polymerisation of many vinyl monomers. The realisation of the advantages of a particular method should apparently depend on the particular problems.

Whatever the nature of different methods of graft polymerisation may seem to be at first sight, in most studies a deviation of the kinetics from the ideal picture for radical polymerisation has been noted[79,90,95-97,101,104-106]. The presence of the filler in the reaction zone exerts a great influence on all the stages of the radical polymerisation regardless of the modification of its surface. In the first place the surface of the filler can influence the rate of decomposition of the peroxide initiator. Thus the acceleration of the decomposition of cumenyl hydroperoxide adsorbed on the surface of refractory titanium compounds (titanium carbide, nitride, carbonitride, and oxycarbonitride as well as the oxides TiO_2 and TiO) has been noted[108]. The decomposition of benzoyl peroxide and azobisisobutyronitrile is influenced only by TiC and TiO_2 respectively. The acceleration of the decomposition of benzoyl peroxide and cyclohexyl peroxydicarbonate has been attributed to the basic nature of the asbestos zeolite[109]. On the other hand Aerosil which has acid properties, does not affect the rate of decomposition of azobisisobutyronitrile[107].

Chemical grafting of peroxy-compounds on the surface of the filler or their fixation in the surface zone leads to a decrease of the mobility of the peroxide molecules and the radicals arising from them and to the formation (in the case of polyfunctional initiators) of strained and less stable cyclic structures. This can result in a significant decrease of E_d for the decomposition reaction[97] and an increase of the rate of decomposition of initiators[95,96].

The fixation of the initiator on the surface hinders the diffusional separation of the radical pair, increasing the probability of the "cage" effect, which is responsible for the decrease of the initiation efficiency, as noted in some investigations[97,108]. For example, when the molecules of 4-azobis-4-cyanopentanoic acid are attached via both ends to the surface of chalk, there is virtually no diffusional separation of the radical pair and the initiation efficiency is low[97].

The localisation of the initiator at the solid surface–liquid interface narrows the initiation reaction zone, increasing simultaneously the concentration of peroxy-groups in this zone. The probability of the recombination of the primary radicals in the surface layer and of the involvement of such radicals in the termination of the growing chains is therefore increased.

Account must be taken of the fact that the efficiency of the initiation of graft polymerisation depends on the concentration of the monomer in the initiation zone, i.e. near the surface. An increase of the monomer concentration in this zone increases the probability of the conversion of primary radicals into growing radicals. The specific features of the surface zone, namely the small difference between the concentrations of the monomer and initiator in this zone, necessitate allowance for the consumption of the monomer in the surface zone during the initiation reaction[110]. This may be the cause of the increase of the reaction order with respect to the monomer noted in a number of instances[101].

Apart from the diffusion-dependent limitations associated with the escape of the radicals from the surface, there can also be difficulties in the transport of monomer molecules to the active centres on the surface. The role of diffusional control increases as the grafted polymer accumulates on the filler surface whereupon the reaction centres are partly shielded by the macromolecules formed. The access of monomer molecules to the polymer phase bound to the surface, formed in the process, becomes hindered and this can then lower the rate of graft polymerisation with increasing degree of conversion[97,101,111]. At the same time, the escape from the surface zone of primary radicals which are not bound to the surface and which are capable of initiating homogeneous polymerisation, occurring simultaneously with the graft polymerisation, is less hindered. The rate of homopolymerisation can therefore be as a rule higher than the rate of graft polymerisation[95,96,101,111]. It is to be expected that the difference between the rates of graft polymerisation and homopolymerisation will be more appreciable when a "poor" solvent is used, in which the transport of the monomer molecules and radicals through the polymer layers grafted to the filler surface is difficult.

Under the conditions of both chemical and adsorption interaction of the monomer with the active surface at low degrees of polymerisation, mesomeric and inductive effects[112-116] as well as orientation effects[93,117] can make a large contribution to the reactivity of the growing radicals. In most cases the changes in the reaction rate constants are in fact accounted for by such factors.

The specific features of radical polymerisation initiated from the surface of the solid phase may consist not only in the diffusional control of the initiation and propagation reactions but also in an increase of the role of the diffusional

control of the chain termination reaction. The restriction of the mobility of macroradicals on their fixation to the surface leads to a sharp fall of the constant k_0.[55] It is therefore of interest to draw an analogy with studies[118,119] devoted to the gel effect in the polymerisation of many monomers. The authors of these investigations attribute the onset of self-acceleration to structure formation in the reaction systems. The polymerisation systems which we have examined and which contain initially an active solid phase constitute even in the first stages of the process a structural network which hinders termination. At the same time the direct involvement of fillers in the chain termination reaction has been stated in a number of investigations[48,69,90,120].

The deviations of the heterogeneous process considered from ideal radical polymerisation, noted in the above studies, indicates the failure of the assumptions of the stationary or quasi-stationary nature of the processes initiated from the surface of the solid phase. It is important to note that polymerisation on the surface frequently entails specific changes in the structure of the polymer chain formed, which affects the properties of the product. A study[121] where it was shown that the radiation-induced polymerisation of acrylonitrile and methacrylonitrile, pre-adsorbed in the form of monomolecular layers on sodium and calcium montmorillonites, leads to the formation of grafted polymers with a cyclic structure is striking in this respect[121]. Such cyclisation proved to be possible as a result of the favourable orientation of neighbouring macromolecules.

A number of studies[122,123] have shown that the method of graft copolymerisation in a mixture of the vapours of monomeric compounds, containing at least one component which is adsorbed selectively on specific functional groups of the support, can be used for the matrix synthesis of copolymer chains with a regular distribution of monomer units specified by the support. The possibility of additional chemical transformations of the monomers under the influence of the surface on which they are fixed has been noted[124]: when polyacrylonitrile grafted to Aerosil was heated *in vacuo* at 200 °C, the amine structure isomerised to the enamine structure as a result of the interaction of the nitrile groups of the polymer and the surface silanol groups with formation of additional polymer–filler chemical bonds.

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The data presented in this review on the physicomechanical, rheological, and other properties of the compositions obtained by the method of polymerisation filling confirm yet again the fact that the formation of a chemical bond between the polymer and the filler tends to improve significantly the properties of the filled compositions as a whole[80,84,85,89,92,93,125–127].

Thus the results of the studies examined in this review demonstrate the likely usefulness of polymerisation filling by radical polymerisation as a method of preparation of filled compositions, the fairly wide variety of the methods investigated, and also the specificity of the reactions involved, whose mechanism has not been ultimately elucidated in a number of instances. The continuation of such studies would therefore be of great interest not only from the standpoint of the optimisation of the filling methods but also as a significant contribution to the study of reactions occurring on solid surfaces. Furthermore, a more detailed investigation of the technological properties of the compositions obtained and their comparison with the properties of polymers filled by the usual methods are necessary.

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Dielectric Methods of Studying the Chemical Bond and the Concept of Electronegativity

S.S.Batsanov

The history and contemporary theories of the polarisation of molecules and crystals are considered and a systematic survey is given of dipole moments and bond ionicities in molecular chemical compounds and also of the effective charges of atoms in crystals. An interpretation of these results is given from the standpoint of the electronegativity concept. Views concerning the effective valencies and coordination numbers of atoms in crystals are considered. Bibliography of 207 references

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I. INTRODUCTION

Polarisation, that is, the separation of charges in an electric field, was the first physical characteristic of molecules which allowed the nature of the chemical bond to be determined quantitatively, and in particular, its degree of ionicity (sometimes termed polarity, from the name of the determining parameter). It is extremely significant that the information which can be extracted from polarisation measurements is unique and constitutes the main component of such structural-chemical characteristics of bonds as dipole moments, effective charges, and valencies of the atoms.

II. POLARISATION AND THE DIPLE MOMENTS OF MOLECULES

In general, molecular polarisation can be represented as:

$$P_m = \frac{M}{\rho}\frac{\varepsilon-1}{\varepsilon+2} = \frac{4}{3}\pi N\left(\alpha + \frac{\mu^2}{3kT}\right), \qquad (1)$$

where P_m is the molecular polarisation, M the molecular mass, ρ the density of the substance, ε the dielectric permittivity, N the Avogadro number, α the polarisability of the molecule, and μ the dipole moment. Clearly, when $\mu = 0$, P_m will be independent of temperature.

A method for the experimental determination of μ follows from Eqn.(1): by measuring P_m at various T the polarisability and dipole moment can be found separately. Information about dipole moments is of independent interest and there is a considerable literature on this subject, which we will not deal with. Table 1 gives the dipole moments of the molecules of the alkali metal, silver, thallium, carbon, and phosphorus halides and also the tin and lead chalcogenides, from Lovas and Tiemann[1].

Since by definition

$$\mu = e^* r , \qquad (2)$$

where e^* is the effective charge on an atom and r the length of a chemical bond, clearly the ratio μ/r should characterise the polarity of the chemical bond (p). In addition to μ, Table 1 gives the ratio $p = \mu/4.8r$.

The second term on the right-hand side of Eqn.(1) corresponds to the orientation part of the total polarisation and is usually denoted by P_0. When a molecule is inserted into an electric field, not only its orientation, but also its deformation—extension of polar atoms in the field direction—take place. This part of the polarisation is termed atomic polarisation, P_a. The deformation of the electronic cloud of the molecule is denoted by P_e. Consequently, the total polarisation consists of P_0, P_a, and P_e. In solids, where $P_0 \cong 0$, we obtain $P_m = P_a + P_e$. Obviously, for non-polar substances $P_a = 0$ and $P_m = P_e$. Hence a comparison of the experimental values of P_a and P_e or of P_m and P_e can give qualitative information about the bond polarity.

Table 1. Dipole moments and bond polarities.

Element	μ, D	p	μ, D	p	μ, D	p	μ, D	p
	F		Cl		Br		I	
H	1.91	0.43	1.08	0.18	0.79	0.12	0.38	0.05
Li	6.33	0.84	7.13	0.73	7.27	0.70	7.43	0.65
Na	8.155	0.88	9.00	0.79	9.12	0.79	9.24	0.71
K	8.59	0.82	10.27	0.80	10.63	0.78	10.82	0.74
Rb	8.55	0.78	10.51	0.78	10.86	0.77	11.48	0.75
Cs	7.88	0.70	10.39	0.74	10.82	0.73	11.69	0.73
Ag	6.22	0.65	5.70	0.52	—	—	—	—
Tl	4.23	0.42	4.54	0.38	4.49	0.36	4.61	0.34
C	1.41	0.22	1.46	0.17	1.38	0.13	1.19	0.12
P	0.77	0.10	0.81	0.08	0.36	0.03	0	0
	O		S		Se		Te	
Sn	4.32	0.49	3.18	0.30	2.82	0.25	2.19	0.18
Pb	4.64	0.50	3.59	0.33	3.28	0.28	2.73	0.22

Despite the qualitative validity of such comparisons the precise relation between the polarisation and the electronic structure of a substance has been found only within the framework of a spectroscopic approach[2,3], which has established a connection between the polarisability of the vibrations of the atom which are taking place and its effective charge (e^*). Some investigators[4-6] used this approach to determine the charges on the atoms in halides of Group IV elements.

Another direction of the work to find bond polarities by a spectroscopic method is based on the measurement of the intensities of infrared absorption bands of molecules to determine e^* as a function of the derivative of the dipole moment with respect to bond length. The history of the problem and the results of the determination of effective charges in Group IV element hydrides have already been given[7].

Hence the spectroscopic values of the atomic charges are also approximate owing to the neglect of a series of factors, namely, anharmonicity and the changes in the orbital overlaps during vibrations, but where molecules are concerned—and consequently the inductive influence of substituents—mainly due to the complexity of the "dipole moment" concept itself.

Without dwelling on the history of the development of theoretical opinions on the nature of dipole moment, we will refer only to Brumer and Karplus's work[8], in which a quantum-mechanical basis was given for the well-known Rittner formula, according to which

$$\mu \simeq er\left(1 - \frac{\alpha_A + \alpha_B}{r^3} + \frac{4\alpha_A\alpha_B}{r^6}\right), \qquad (3)$$

where α_A and α_B are the polarisabilities of ions A and B.

The last theoretical investigation of the dipole moments of ionic molecules is that of Matcha and King[9], who took into account not only effective charges and the polarisability of atoms, but also the moments of the orbital overlaps and the repulsion of the electron clouds. The experimental values of e^* determined in that work[9] are given in Table 2; extrapolated values of the charges on the atoms are also given there (in parentheses).

Table 2. Charges of the atoms in alkali halide molecules.

A	B			
	F	Cl	Br	I
Li	0.87	0.82	(0.79)	(0.76)
Na	0.89	0.86	0.84	0.81
K	0.93	0.91	(0.89)	(0.86)
Rb	0.94	0.92	(0.90)	(0.87)
Cs	0.99	0.96	(0.94)	(0.91)

The relation between the bond polarity (p.1202) and e^* [9] is expressed by the formula:

$$e^* \simeq p\left(1 - \frac{\alpha_A + \alpha_B}{r^3}\right)^{-1}. \qquad (4)$$

Hence it is clear that the reduced value of p in CsF in comparison with other alkali metal fluorides (cf. Table 1) is due to the greater polarisability of the caesium ion.

As for the dipole moments of covalent bonds, Mulliken[10] found by LCAO MO theory that the dipole moment consists of three terms: the ionic moment, $\pm e^* r$; a covalent term, $\mp 4eabs$ where a and b are the weighting factors of the atomic wave functions, and S is the overlap integral; and the moment of the isolated electron pair, $\pm\mu_S$.

The next broad step on the theory of dipole moments was taken by Coulson[11], who, by analysing the charge distribution in the C–H bond by the MO method, concluded that for hybrid orbitals in addition to the three Mulliken terms allowance must be made for the hybridisation moment.

Hence bond ionicities can only be calculated from measured dipole moments if the remaining components of the bond moment are determined empirically or theoretically. Therefore subsequently in addition to the accumulation of new experimental results the main attention was directed at these particular problems[12–18].

III. BOND IONICITY AND ELECTRONEGATIVITY OF ATOMS IN MOLECULES

Since in general the charges on atoms cannot be determined in the simplest manner—by Eqn.(2)—Pauling proposed that the variation of bond ionicity† with the electrochemical properties of its component atoms be found and then the charges determined directly from these characteristics of the atoms.

The concept Pauling used as such a property was the electronegativity of an atom, that is, its ability to attract valence electrons. The history of this[19–22] will not be discussed here other than to point out that electronegativity can be determined:

(1) from thermodynamic data by the equation:

$$X_A - X_B = E(A-B) - \frac{1}{2}[E(A-A) + E(B-B)], \qquad (5)$$

where X_A and X_B are the electronegativities of the atoms A and B, and E(A–A), E(A–B), E(B–B) are the A–A, A–B, and B–B bond energies.

(2) from ionisation potentials and electron affinities:

$$X = \frac{1}{2}(I + A), \qquad (6)$$

where I is the first ionisation potential and A the affinity for one electron of the atom in the valence state;

(3) from the covalent radii (r) and effective nuclear charge (z^*):

$$X = az^*/r^b + c; \qquad (7)$$

(4) from the spectroscopic characteristics of the bonds between the atoms:

$$k = a(X_A X_B/r^2)^b + c \text{ or } \Delta X_{AB} = m\nu_{AB} + n, \qquad (8)$$

where k is the force constant of the bond; ν the characteristic frequency of the vibrations of the bond A–B; and a, b, c, m, and n are constants.

The literature on the determination and use of atom electronegativities is so great that it cannot be cited completely in a journal paper. Therefore we will quote only the principal, mainly review, papers plus investigations carried out after 1968.

Thermochemical determinations of electronegativity based on Pauling's equation, Eqn.(5), have been carried out[23–26]; the averaged results of these studies are given in the first sub-lines of Table 3.

Electronegativities have been determined with Mulliken's equation, Eqn.(6).[27–39] The ionisation potentials of atoms in the valence state cannot be determined experimentally when the valence state does not coincide with the ground state, since then a knowledge of the promotion energies of the electrons is required. Consequently most studies in this direction are quantum-mechanical. The ideas of the electronegativity of an atom depending on the orbital type of its bonds ("the orbital electronegativities of atoms") arose in this particular region.

† Bond ionicity is essentially a synonym for the effective charge of an atom; the ionicity is usually expressed in percentages of the formal charge, the effective charge in fractions of the electronic charge.

Table 3. Electronegativities of the atoms in molecules, determined by various methods.

Period	1A	2A	3A	4A	5A	6A	7A	8A	1B	2B	3B	4B	5B	6B	7B
II	Li 1.0 0.9_5 0.9 0.9_5	Be 1.5 1.4 1.4_5 1.4_5									B 2.0 1.9 1.9 1.9	C 2.6 2.4 2.4_5 2.5_5	N 3.0 2.8 3.0 3.0	O 3.5 3.3_5 3.4_5 3.4_5	F 4.0 3.9_5 4.0 3.9_5
III	Na 0.9 0.9 0.9 0.9	Mg 1.3 1.2 1.2 1.2									Al 1.6 1.6 1.4 1.5	Si 1.8 2.0 1.7 1.8	P 2.1 2.2 2.0_5 2.1	S 2.6 2.5 2.5 2.5	Cl 3.1 2.9 2.9 3.0
IV	K 0.8 0.8_5 0.8 0.8	Ca 1.0 1.1 1.0 1.0	Sc 1.3 1.3 1.3 —	Ti 1.5 1.5 1.5 2.0	V (III) 1.7 1.5 1.7 2.0	Cr (III) 1.9 1.6 1.7 2.0	Mn (III) 1.7 1.7 1.8 2.2	Fe (III) 1.9 1.7 1.9 2.3	Co (III) 2.0 1.8 2.0 1.8	Ni (III) 2.0 1.9 2.1 2.0	Cu 1.9 1.6 1.8 2.2	Zn 1.6 1.5_5 1.8 1.4	Ga 1.7 1.7 1.9 1.4	Ge 1.9 2.1_5 2.0_5 1.7	As 2.0 2.2 2.2 2.0	Se 2.5 2.4 2.5 2.4	Br 2.9 2.7 2.7_5 2.7_5
V	Rb 0.8 0.8 0.8 0.8	Sr 1.0 1.0 1.0 1.0	Y 1.2 1.2 1.2 —	Zr 1.4 1.4 1.4_5 1.6	Nb (III) 1.6 1.3 1.6_5 —	Mo (IV) 2.0 1.7 1.7 1.9	Tc (IV) 1.9 1.6 1.8 2.2	Ru 2.2 1.8 2.0 2.0	Rh 2.2 1.9_5 2.1 2.3	Pd 2.2 2.0_5 2.1 —	Ag 1.9 1.4 1.7 1.9	Cd 1.7 1.4 1.7 1.4	In 1.8 1.6 1.8 1.4	Sn (II) 1.8 2.0 1.9 1.7	Sb (III) 1.9 1.9 2.0 1.8	Te 2.1 2.2 2.2 2.1	I 2.6 2.6 2.4 2.4_5
VI	Cs 0.7_5 0.7 0.8 0.7_5	Ba 0.9 0.9_5 1.0 0.9	La 1.1 1.2 1.2 —	Hf 1.3 1.4 1.6 1.5	Ta (III) 1.5 1.4 1.8 —	W (IV) 2.0 1.7 1.9 1.7	Re (IV) 1.9 1.6 2.0 2.0	Os 2.2 1.9_5 2.1 2.2	Ir 2.2 2.1 2.2 2.2	Pt 2.2 2.1_5 2.2 2.3	Au 2.4 1.6 2.0 3.1	Hg 1.9 1.5 1.9 1.5	Tl (III) 2.0 1.6 1.9 1.3	Pb (II) 1.9 1.9 1.9 1.5	Bi (III) 1.9 1.8 2.0 1.8	Po 2.0 1.9_5 2.1 —	At 2.2 2.4_5 2.3 —

Table 4. System of the electronegativities of the atoms in molecules*.

Period	1A	2A	3A	4A	5A	6A	7A	8A	1B	2B	3B	4B	5B	6B	7B
II	Li 0.9_5	Be 1.5									B 1.9	C 2.5	N 3.0	O 3.5_5	F 4.0
III	Na 0.9	Mg 1.2									Al 1.5	Si 1.9	P 2.1	S 2.5	Cl 3.0
IV	K 0.8	Ca 1.0	Sc 1.3	Ti 1.6	V (II) 1.5 (III) 1.7 (V) 2.0	Cr (II) 1.6 (III) 1.8 (VI) 2.2	Mn (II) 1.5 (III) 1.8 (IV) 2.0 (VII) 2.3	Fe Co Ni (II) 1.8 1.8 1.9 (III) 1.9 2.0 2.0 (IV) — 3.1 3.4	Cu (I) 1.8 (II) 2.1	Zn 1.6	Ga 1.7	Ge 2.0	As 2.0	Se 2.4	Br 2.8
V	Rb 0.8	Sr 1.0	Y 1.2_5	Zr 1.5	Nb (III) 1.6 (V) 1.9	Mo (IV) 1.8 (VI) 2.2	Tc (IV) 1.9	Ru Rh Pd (II) 2.0 2.0 2.1 (III) 2.1 2.1 — (IV) 2.2 2.2 2.3	Ag 1.9	Cd 1.7	In 1.8	Sn (II) 1.8 (IV) 2.0	Sb (III) 1.9 (V) 2.2	Te 2.1	I 2.5
VI	Cs 0.7_5	Ba 0.9	La 1.2	Hf 1.4	Ta (III) 1.5 (V) 1.8	W (IV) 1.8 (VI) 2.1	Re (IV) 1.9	Os Ir Pt (II) 2.0 2.1 2.2 (III) 2.1 2.2 — (IV) 2.3 2.3 2.4	Au (I) 2.0 (III) 2.4	Hg 1.8	Tl (I) 1.4 (III) 1.9	Pb (II) 1.9 (IV) 2.1	Bi (III) 1.9 (V) 2.2	Po 2.0	At 2.2
VII	Fr 0.7	Ra 0.9	Ac 1.1												
Actinides				Th (IV) 1.3	Pa (IV) 1.3 (V) 1.5	U (IV) 1.4 (V) 1.6 (VI) 1.8									

*$X_M = 2.1$.

Many investigators regard the determination of electronegativities from ionisation potentials as the most substantiated physically. Consequently the difference in the dimensionalities of the thermochemical and ionisation electronegativities was thought[40] to be a defect of the electronegativity concept. However, Martynov and Batsanov[37] have shown that the use of not the first ionisation potential but the mean value of the potential for all the outer electrons ($\bar{I}$) leads to an equation of the type:

$$X = a(\bar{I})^{1/2} + b \quad , \qquad (9)$$

where X has the same dimensionality as the thermochemical electronegativity of the atoms. The ionisation electronegativities are given in the second sub-lines of Table 3.

Calculations of the electronegativities of the atoms from their radii and the effective charges of the atomic nuclei by equations of the type of Eqn.(7) also have a history of many years and are continuing vigorously to the present time[41-50]. Averaged electronegativities from these studies are given in the third sub-lines of Table 3.

Spectroscopic determinations of electronegativities are based either on the use of the force constants of the bonds[51,52] or the wavenumbers of the vibrations in the

ultra-violet[53–59] infrared[60–64], or radio-wave[65–67] regions of the spectrum, or chemical shifts in the Mössbauer spectra[68,69]. The averaged atomic electronegativities from optical spectroscopic results are given in the fourth sub-lines of Table 3.

As Table 3 shows, the results of the electronegativity calculations by various methods agree very well, which allows a universal system of electronegativities of the elements to be constructed. Table 4 gives such a system for the atoms in various oxidation states.

Pauling deduced the following relation from a comparison of the dipole moments and electronegativities of the atoms[23]:

$$i = 1 - e^{-a\Delta X^2}, \qquad (10)$$

where a is a constant, which, determined after refinement of the dipole moment of HF, equals 0.18. Analysis of Eqn.(10) and confirmation of its validity by independent methods are considered in a book[19].

Nethercot[70] recently took the next step in the direction of the formal development of Eqn.(10). He suggested that i should be expressed as a function not of ΔX but of the normalised difference in the electronegativities of the atoms:

$$i = 1 - e^{-a\Delta \bar{X}^2}, \qquad (11)$$

where

$$\Delta \bar{X} = \Delta X/(X_A X_B)^{1/2}.$$

The successful solution of the problem of finding i from ΔX (using the dipole moments of the HHal molecules) allowed the reverse problem to be solved also—the finding of μ (for example, for organic molecules) from the electronegativity and i.[71]

IV. POLARISATION OF CRYSTALS: BORN AND SZIGETI'S THEORETICAL APPROACH

The development of the theory of polarisation of ionic crystals began with the well-known equation of Born and Göppert-Meyer, in which the dielectric permittivity is linked with the natural frequency of the transverse lattice vibrations:

$$\varepsilon = n^2 + \frac{4\pi(ze)^2}{\omega_i^2 \bar{M} V}. \qquad (12)$$

Here ω_i is the frequency of the transverse lattice vibrations, V the volume associated with one particle, $\bar{M}$ the reduced mass of the vibrating particle, n the refractive index, and z the valency of the ion.

Comparison of the experimentally measured and theoretical (calculated from the Born formula) values of ε showed that usually the calculated ε were less than the experimental values. The reason for the discrepancy between theory and experiment is in the assumption, made in the theory, that the interaction of the ions is coulombic and that P_a and P_e are additive. Actually, the electron clouds of the ions in the crystals are deformed and are overlapped during the vibrations of the lattice, as a result of which the atomic and electronic components of the polarisation are no longer independent additive quantities.

Szigeti[72] showed that the deformation of the electron cloud of the ions due to the transverse vibrations of the lattice increases the atomic polarisation. On taking into account also that the field strength E in the dielectric is less than the external field due to the polarisation of the specimen, Szigeti obtained the following equation:

$$\varepsilon = n^2 + \frac{4\pi(ze)^2}{\omega_i^2 \bar{M} V}\left(\frac{n^2+2}{3}\right)^2. \qquad (13)$$

The Szigeti equation differs from the Born formula by the factor $[(n^2+2)/3]^2$, which takes into account the contribution from electronic polarisation to atomic polarisation. This term plays a greater part the higher the refractive index, that is, the greater the covalency of the bond; it is in just these circumstances that Born's assumption that isolated ions are not deformed is least valid.

Comparison of the result of calculations by Eqn.(13) with experiment showed that the calculated values of ε are always greater than those measured experimentally. This led Szigeti to the idea of changing the formal charge of the ion z to some quantity s which characterises the departure of the actual charge e^* from the theoretical value. It is easy to see that in the physical sense the parameter s is the effective charge of the atom: $s = e^*$. On taking into account that

$$\omega_t = 2\pi\nu_t,$$

where ν is the experimentally determinable linear transverse vibration frequency of the lattice, Szigeti deduced that

$$e^* = \frac{3\nu_t c}{ze\,(n^2+2)}[\pi(\varepsilon - n^2)\bar{M}V]^{1/2}. \qquad (14)$$

where e^* is the effective charge of the atom, which reflects the bond ionicity in the crystal.

Hence on the basis of characteristics of the crystal such as its molecular mass, volume, the frequency of the vibrations of the atoms the dielectric permittivity, and the refractive index, the Szigeti equation allows the departure of the bond character from the purely ionic state to be determined.

Table 5. Effective charges of the atoms in crystals of type AB (according to Szigeti).

AB	e^*/z	Reference	AB	e^*/z	Reference	AB	e^*/z	Reference
LiH	0.53	74	CuO	0.54	79	PbO	0.58	93
LiF	0.81	75	BeO	0.55	80	PbS	0.36	83
LiCl	0.78	75	MgO	0.59	79	PbSe	0.35	79
LiBr	0.74	75	MgS	(0.62) **	79	PbTe	0.28	79
LiI	0.54	75	CaO	0.61	81	MnO	0.55	79
NaF	0.83	75	CaS	0.52	79	α-MnS	0.44	94
NaCl	0.77	75	SrO	0.61	81	γ-MnS	0.35	94
NaBr	0.75	75	SrS	0.53	79	MnSe	0.42	94
NaI	0.74	75	BaO	0.74	81	MnTe	0.33	94
KF	0.92	75	BaS	0.55	79	FeO	0.46	79
KCl	0.84	75	ZnO	0.60	82	CoO	0.44	79
KBr	0.77	75	ZnS	0.44	82	NiO	0.41	79
KI	0.75	75	ZnSe	0.40	82	BN	0.30	95
RbF *	0.97	75	ZnTe	0.39	82	BP	0.25	96
RbCl	0.84	75	CdO	0.59	83	AlN	0.41	83
RbBr	0.80	75	CdS	0.45	82	AlP	0.26	83
RbI	0.77	75	CdSe	0.42	82	AlAs	0.21	83
CsF *	0.96	75	CdTe	0.38	82	AlSb	0.16	83
CsCl	0.85	75	HgO	0.57	79	GaN	0.41	83
CsBr	0.82	75	α-HgS	0.20	84	GaP	0.19	83
CsI	0.78	75	β-HgS	0.28	85	GaAs	0.17	83
CuCl	0.98	76	HgSe	0.27	86	GaSb	0.13	83
CuBr	0.96	76	HgTe	0.26	87	InP	0.22	83
CuI	0.91	76	EuO	0.67	88	InAs	0.18	83
AgF	0.89	77	EuS	0.54	89	InSb	0.14	83
AgCl	0.71	77	EuTe	0.50	90	SiC	0.22	83
AgBr	0.67	77	SnS	0.33	79			
AgI	0.61	77	SnSe	0.27	91, 92			
TlCl	0.88	77	SnTe	0.26	83			
TlBr	0.84	77						
TlI	0.83	77						
HgCl	0.70	78						

* Charges of the atoms recalculated according to the X-ray densities[97].

** Estimated value.

The Szigeti equation was used initially to calculate the effective charges of the atoms for only simple cubic crystals, but as time elapsed more and more complex crystalline compounds were studied, both isotropic and anisotropic. The

development of the Szigeti method is linked with the perfection of the measuring techniques and with the refinement of the method of calculating the optical characteristics of anisotropic crystals.

Most anisotropic crystals are characterised by infrared spectra so complex that the choice of the frequencies of the transverse and longitudinal vibrations—ν_t and ν_l—for calculation of charges is a special problem. This has been considered by Loudon[73] for uniaxial crystals as example. It was found that usually some of the bands in the infrared reflection spectra of the uniaxial crystals hardly shift on going from the orientation of the electric field parallel to the c axis towards a perpendicular orientation, that is, $\nu_\parallel \cong \nu_\perp$. If the inequality

$$|\nu_\parallel - \nu_\perp|_{t \text{ or } l} \ll (\nu_l - \nu_t)_{\parallel \text{ or } \perp}, \qquad (15)$$

holds in this, then these bands correspond to isotropic oscillators, since the internal field is then analogous to the field of the cubic crystals. Here it has been shown[73], that the strength of the isotropic field is a maximum for the highest frequency vibrations which satisfy inequality (15).

Tables 5 and 6 give the results of experimental investigations on crystalline compounds by the Szigeti method. The literature reference in Tables 5 and 6 are usually for the latest papers on these compounds, which have been studied repeatedly, or for those papers in which there are the most accurate physical characteristics of the crystals, although the calculations of effective charges were not carried out.

Table 6. Bond ionicities in crystals of type A_nB_m (according to Szigeti).

Substance A_nB_m	e^*/z	Reference	A_nB_m	e^*/z	Reference	A_nB_m	e^*/z	Reference
MgF_2	0.76	98,99	CoF_2	0.74	99	$HfSe_2$	0.45	116
CaF_2	0.84	100,101	$CoCl_2$	0.41	107	MoS_2	0.06	117
SrF_2	0.85	102	$CoBr_2$	0.40	107	$MoSe_2$	0.04	118
$SrCl_2$	0.76	103	NiF_2	0.68	99]	ThO_2	0.60	119
BaF_2	0.87	102	$NiCl_2$	0.40	107	UO_2	0.58	119
ZnF_2	0.76	98,99	$NiBr_2$	0.35	107	CeO_2	0.48	120
CdF_2	0.83	104	NdOF *	0.76	108	ScF_3	0.76	121
$CdCl_2$	0.72	104	Na_2S	0.58	109	YF_3	0.76	108, 121
$CdBr_2$	0.69	104	Cu_2O	0.29	110	LaF_3	0.74	108
CdI_2	0.67	104	TiO_2	0.60	111	AlF_3	0.60	121
HgI_2	0.38	105	TiS_2	0.39	112	GaF_3	0.60	121
EuF_2	0.84	106	$TiSe_2$	0.18	112	InF_3	0.61	121
PbF_2	0.95	104	SiO_2	0.60	111	Y_2O_3	0.62	120
$PbCl_2$	0.90	104	GeO_2	0.54	111	Y_2S_3	0.40	122
PbI_2	0.75	104	GeS_2	0.18	113, 114	La_2O_3	0.62	108
MnF_2	0.81	99, 101	$GeSe_2$	0.17	92]	La_2S_3	0.40	122
$MnCl_2$	0.50	107	SnO_2	0.57	111	Al_2O_3	0.59	111
$MnBr_2$	0.50	107	SnS_2	0.32	115	Cr_2O_3	0.46	111
FeF_2	0.68	98]	$SnSe_2$	0.25	115	As_2S_3	0.20	123
$FeCl_2$	0.42	107	ZrS_2	0.44	116	As_2Se_3	0.14	123
$FeBr_2$	0.41	107	HfS_2	0.50	116			

* Since the atoms O and F have similar sizes and masses, these compounds are close to type AB_2.

Table 5 allows a series of conclusions to be drawn. The values of e^* increase with the difference in the electronegativities of the atoms A and B, and also with the coordination numbers of the atoms in the crystal structures. Thus going from α- to β-HgS is accompanied by an increase in the number of nearest neighbours from 2 to 4, and for α- and γ-MnS the coordination numbers are changed from 6 to 4. The bond ionicity increases with the coordination of the atoms, which is in complete agreement with Pauling's postulate[23]. It should also be noted that the difference in the bond ionicities of analogous compounds of the elements of the A and B subgroups was significantly less than could be expected from a comparison of the electronegativities of atoms in molecules (Table 4).

Table 6 gives the results of studies on crystalline compounds of type A_nB_m by the Szigeti method. When the values of e^* in the papers cited were calculated by the Born equation they were recalculated by Eqn.(14). In the treatment of the published data for MnF_2, Cu_2O, GeS_2, and $GeSe_2$ the choice of the lattice vibration frequencies was made with allowance for Eqn.(15).

The data in Table 6 agree with the changes in the electronegativities of the atoms but there are significant discrepancies for several compounds. Thus the bond ionicities in the Pb halides are very high, which Axe and coworkers[124] explained by the increased valency of lead in these compounds; the bond ionicities in the molybdenum chalcogenides were unexpectedly low, which Lucovsky and coworkers[116] explained by the formation in this instance of the radicals S_2 and Se_2, the oxidising abilities of which are considerably lower than those of S and Se atoms.

The low bond ionicity for copper(I) oxide compared with copper(II) oxide (and with the calculation by the electronegativity method) must show a decrease in the effective valency of copper in Cu_2O. We will return to the problem of effective valencies; here we will only note that according to X-ray diffraction studies[125], there is a Cu–Cu bond in Cu_2O.

Not only binary compounds, but also double salts and complexes have been studied by the Szigeti method. In every instance it was found that the ionicity of the bonds in the inner sphere of complexes is higher than that in the corresponding binary compounds.

Analysis of the infrared spectra of binary oxides and complexes allows the Szigeti equation to be used for determining the effective charges not only on ionic complexes but also in the inner sphere of these complexes. Table 7 gives the results of investigations of the effective charges of the atoms in complexes[111,126,127].

Table 7. Effective charges of the atoms in oxygen compounds.

M_nAO_m	e^*/z (M)	e^*/z (A)	e^*/z (O)	M_nAO_m	e^*/z (M)	e^*/z (A)	e^*/z (O)
$NaNO_3$	0.92	0.04	0.18	$SrTiO_3$	0.80	0.71	0.75
$RbClO_3$	0.90	0.16	0.28	$BaTiO_3$	0.82	0.64	0.70
$MgCO_3$	0.67	0.11	0.26	$PbTiO_3$	0.85	0.53	0.62
$NdAlO_3$	0.84	0.40	0.62	$LiNbO_3$	0.77	0.62	0.64
Be_2SiO_4	0.65	0.46	0.55	$LiTaO_3$	0.79	0.67	0.69
Mg_2SiO_4	0.73	0.42	0.58	$CaMoO_4$	0.80	0.42	0.52
$ZrSiO_4$	0.83	0.38	0.60	$CaWO_4$	0.82	0.47	0.56

Comparison of the results in Tables 5–7 shows that in compounds of the M_nEO_m type the ionicity of the M–O bond is greater, and that of the E–O bond less, than in the corresponding binary oxides of M and E. Such a distinctive compensation dependence in the ratio of various properties of complexes is constantly encountered.[128] It has been shown by the Szigeti method that there is an analogous dependence for solid solutions of binary compounds, for example, in mixed alkali halides[129].

As the KCl concentration in KCl–KBr solid solution is reduced the frequency of the vibrations and the crystal cell volume will vary monotonically from the values characteristic of KCl to those characteristic of pure KBr; the reduced

mass M also changes analogously. In addition, a peculiarity of the Szigeti equation is that the relation

$$\nu_t \sqrt{\overline{M}V} = \text{const} \quad (16)$$

is valid. This follows from the theory of a harmonic oscillator and the calculation of a force constant according to Coulomb's law. Therefore changes in the reduced mass (or molar volume) are compensated by a change in the vibration frequency, that is, for low concentrations of KCl in KCl–KBr solid solution the values of ν_t, $\overline{M}$, and V for pure KBr can be inserted into the Szigeti equation.

On considering the characteristics of an individual KCl particle in a continuous matrix of KBr, it must be assumed that the value of ε for such a solid solution will be the same as for pure KBr, since the dielectric permittivity in its physical essence relates to the medium in which this particle is located. As for the refractive index, that depends on the change in the volume of the KCl particle in the solid solution compared with the free state.

Without dwelling on the details of the calculation of the optical dielectric constants (cf. Batsanov[129]) we will pass to a statement of the results of applying the Szegeti method to the determination of the effective charges of atoms in solid solutions. Table 8 gives the bond ionicities for infinitely dilute solid solutions; in real materials there will be an intermediate situation.

Table 8. Effective charges of the atoms in pure and mixed crystals [solid solutions] MHal.

M	Initial substance MCl	Solid solution MCl–MBr		Initial substance MBr
Li	0.74	0.83	0.59	0.71
Na	0.76	0.85	0.60	0.72
K	0.80	0.88	0.67	0.77
Rb	0.85	0.89	0.72	0.80
Cs	0.86	0.92	0.72	0.81
Hal	KHal	KHal–RbHal		RbHal
F	0.93	0.90	1.00	0.95
Cl	0.80	0.76	0.92	0.85
Br	0.77	0.72	0.88	0.80
I	0.74	0.69	0.86	0.78

As Table 8 shows, the difference in the bond ionicities of the components of the solid solution is increased in the formation of a mixed crystal: the bond in the more ionic crystal becomes even more ionic, that in the less ionic becomes more covalent. The oppositely directed changes in the character of the chemical bonds of the components of the solution lead to the mutual compensation of a large part of these changes, but in all examples the integral effect is never zero; here solid solutions differ from mechanical mixtures.

It is extremely important that the opposing changes in the charges of the atoms entering into the composition of the components of the solid solution lead to the spatial approach of the atoms, which is responsible for the possible formation of a stable solution. In addition, the compensation nature of the variation of the effective charges and radii of the atoms in the solid solution leads also to compensation of the energies of the various chemical bonds, which appears thermochemically in the low enthalpies of formation of solid solutions (which, incidentally, are not equal to the simple difference of the standard bond energies of the atoms participating in the formation of the solid solution).

It is extremely tempting to study the change in the nature of the chemical bond in crystals as the thermodynamic conditions are varied, since all the components of the Szigeti equation can be determined experimentally. However, complete certainty has not been acheived even in the sign of the change in the charge on an atom as the volume of the crystal is varied. In fact, an increase in the volume of a crystal during heating should lead to a decrease in the overlap of the atomic orbitals (and consequently to an increase in the charges on the atoms), but since this increase in volume takes place due to the increase in the amplitude of the vibrations of the atoms, there should be an increase in the overlap of the electron orbitals. Hence the total change in the character of the chemical bond during the heating of the crystal should be small and, generally speaking, can be of either sign[100,130–132].

V. EFFECTIVE CHARGES AND ELECTRONEGATIVITIES OF ATOMS IN CRYSTALS

The problem of the determination of the effective charges of atoms in a molecule or in a crystal reduces to the separation of that fraction of the space in the crystal or molecule in which the calculation or measurement of the electron density of the atoms is carried out. The minima on the curves or surfaces of electron density distribution can serve as a criterion of the division of the space into atomic regions[133–135]. A comparison of the effective charges, that is, of the difference in the formal and real numbers of electrons in the region of a given atom, determined by X-ray diffraction, with the independent determination of e* gives good agreement[21,135].

Mulliken and coworkers[136–138] developed a quantum-chemical approach to the determination of the electron density of a chemical bond; calculation by the Hartree-Fock method of the electron densities of isolated atoms and of the appropriate compounds including these atoms in their composition allows the fine peculiarities of the chemical bond to be found by comparison. Essentially, the change in the electron density distribution in the formation of covalent molecules does not exceed 10% in comparison with the isolated atoms[139], and the charge transfer (from the metal to the non-metal atom) in polar molecules correlates with the difference in the electronegativities of these atoms[140].

The problem of the theoretical calculation of the effective charges of atoms in crystals has been considered in detail in many monographs on quantum chemistry and even in simple listing of these studies would take up much space. We are therefore limited to references to the main reviews in this field, in which either original approaches are reported or summaries are given of appropriate investigations, mainly from published results. First of all there are the classical books of Pauling[23], Coulson[141], and Slater[142], but there are others[41,135,143–148].

The most important result of the numerous theoretical investigations is that despite all the stipulations and limitations the concept of "effective charge of an atom in a crystal" plays an important part in structural chemistry and allows not only many physicochemical properties of crystals to be explained but also new properties to be predicted.

In this review we will consider only those studies in which the problem of the effective charges of atoms in crystals was studied from the viewpoint of dielectric methods and the concept of electronegativity, based on this approach.

The first quantitative estimate of the charges of the atoms in crystals from results for corresponding molecules was proposed by Pauling[23]. According to him, the covalency of the

bond in the crystals will be the same fraction of the covalency in the corresponding molecules as the valency of the atoms (z) is of the coordination number (N_C):

$$i = 1 - \frac{z}{N_c} e^{-a\Delta X^2} \quad . \qquad (17)$$

This rule was confirmed by an analysis of the interatomic distances in molecules and crystals, by comparison of the bond ionicities in molecules and crystals, in the X-ray spectroscopic and photoelectronic study of the chemical bond in crystalline compounds.

As he showed himself, Pauling's rule is valid, however, only for compounds of cations of the noble gas type, since the atoms of the B subgroups can form a larger number of bonds than their valency. Additional bonds in crystalline compounds are formed by the free orbitals of the metal atoms and the unpaired electrons of the non-metal atoms. In addition, the change in N_e on going from the isolated molecules to the crystalline state is accompanied by a change in the polarisation interaction of the ions; for crystals of the alkali halides this change is responsible, for example, for 50–80% of the total e*.[149]

Therefore for calculating the total electron density on the atoms in crystals it was proposed to take into account not only the coulombic but also the ion-dipole interaction of atoms on the basis of the ionisation potentials and the electron affinity for the valence state[19,150]. Comparison of degrees of bond ionicity thus calculated with the experimental values shows satisfactory agreement[150].

Sanderson[151,152] proposed an original method for determining bond ionicities in molecules. He suggested that the electronegativities of the atoms, or, more precisely, quantities proportional to them, the "stability ratios" S are given by:

$$S = N/qr^3 \qquad (18)$$

where N is the atomic number of the element, r the covalent radius, and q a constant, will be equalised in the formation of molecules. Hence the relation of the stabilities of the atom in the molecule AB is

$$S_{AB} = (S_A S_B)^{1/2} \quad . \qquad (19)$$

Knowing the set of covalent and ionic S, the degree of ionicity of a bond can be calculated by the equation:

$$i = (S_{AB} - S_A)/(S_{A+} - S_A) \quad . \qquad (20)$$

Comparison of the degrees of ionicity calculated by the Sanderson and Pauling methods shows a statistical mean deviation of ~10%.

The Sanderson method was developed for the calculation of the bond ionicities of molecular compounds of complicated composition[41,153,154]. The quantum-chemical aspect of the Sanderson method was developed by many investigators and these investigations were surveyed by Jolly and Perry[155].

A variant of the Sanderson method suitable for calculating bond ionicities in coordination crystals was proposed recently[156]. This consists essentially in the calculation of S of the atoms A and B in crystals AB by the equation:

$$\bar{S}_A = (S_A \cdot S_B^{\alpha})^{1/(\alpha+1)} \text{ or } \bar{S}_B = (S_B S_A^{\alpha})^{1/(\alpha+1)} \quad , \qquad (21)$$

where α is the reduced Madelung constant.

Then $\bar{S}_A$ and $\bar{S}_B$ are compared with the values of S of the same atoms in the purely ionic and purely covalent bonds in the crystalline state with the aid of an equation of type (20), since the effective charges for cation A and for anion B in the crystal AB should equal one another.

Table 9 gives, as an example, the results of calculating the effective charges of the atoms in alkali halides (cf. Batsanov[156]). The agreement of these results with the independently determined effective charges of the atoms is also rather good, which indicates the correctness of the method of calculation and the objective significance of the effective charges themselves.

Table 9. Effective charges of the atoms in crystals calculated by the method of equalising S.

AB	e^*_A	e^*_B	AB	e^*_A	e^*_B
NaF	0.92	0.92	RbF	0.98	0.95
NaCl	0.80	0.82	RbCl	0.85	0.85
NaBr	0.76	0.79	RbBr	0.81	0.82
NaI	0.63	0.68	RbI	0.69	0.71
KF	0.95	0.94	CsF	0.99	0.96
KCl	0.83	0.83	CsCl	0.87	0.86
KBr	0.79	0.80	CsBr	0.83	0.83
KI	0.66	0.69	CsI	0.71	0.72

However, such a position occurs only for ideal crystal structures of the type of ZnS, NaCl, CsCl, etc., in which the coordination number (C.N.) is known precisely. When the coordination polyhedron is distorted, the distances from the centre to the various vertices in it differ appreciably, which raises the question of how the C.N. is to be used in calculating the bond ionicity. The difficulty in choosing the C.N. for calculating bond ionicities in crystals with irregular coordination polyhedra has been discussed in the literature.[108,157]

The escape from this position can be twofold: either the theoretical calculation of effective C.N. taking into account the non-equivalence of the bonds between the central atom and various ligands[158–163], or an empirical allowance for the real coordination of the atoms in the crystal. In the latter approach we[164] used the sublimation energy of the crystal (ΔH_S), since it is just this that distinguishes a molecular from a crystalline compound. Use of the sublimation energy permits going from the electronegativity of atoms for molecules to the electronegativities of atoms for crystals (X^*). To do this the well-known Pauling equation:

$$\Delta X_{AB} = 0.208\,[\Delta E(AB)]^{1/2}$$

is transformed into the form:

$$\Delta X^*_{AB} = 0.208\,[\Delta E(AB) + \Delta H_s]^{1/2} \quad . \qquad (22)$$

Combination of this equation with formula (5) gives the following expression:

$$\Delta\Delta X = \Delta X^*_{AB} - \Delta X_{AB} = 0.208\{[\Delta E(AB) + \Delta H_s]^{1/2} - [\Delta E(AB)^{1/2}]\} \quad , \qquad (23)$$

which allows the difference in the electronegativities of the atoms for the molecular and crystalline states to be calculated, and hence also the electronegativity of the atom for the crystalline state if the problem of which of the partners in the bond A–B is responsible for the change in electronegativity on going from the molecular to the crystalline state can be solved. Since the enthalpies of sublimation of the elements playing the part of anions are significantly less than those of metals, clearly the influence of the ΔH_S should appear mainly on the electronegativity of the cation. The results of such calculations of the electronegativities of the atoms in crystals have been given[164].

The electronegativities of the atoms in crystals can also be calculated from the electronic work function (Φ). Stevenson[165] suggested that the electronegativities of atoms of metals in the crystalline state could be calculated by the equation:

$$X^* = 0.355\Phi \quad . \qquad (24)$$

Later[166] the coefficient in Eqn.(24) was changed to 0.318 and the electronegativities of the atoms of almost all metals in the crystalline state were calculated. It was found that electronegativity$_{met}$ < electronegativity$_{mol}$, which is explained by the greater screening of the nuclear charge of atoms in the solid state compared with that of an atom in a molecule.

The closest approaches to thermodynamic values of the electronegativities of atoms in the crystalline state are obtained in calculations with the formula:

$$X^* = 0.4\Phi - 0.5 \quad . \qquad (25)$$

The values of the electronic work function for pure metals corrected from the enthalpies of formation of intermetallic compounds were used[167-172] for interpreting the structure and properties of metallic phases.

In using methods of calculating the electronegativities of atoms in crystals starting from geometric considerations, then in equations of type (7) instead of the usual covalent radius it is necessary to use the covalent radius of the same atom for the crystalline state and to allow also for the bond multiplicities in coordination crystals (cf. Batsanov[164]). The calculation of the electronegativities of atoms in crystals by a method similar to that of Sanderson but based on Fermi statistics has also been described; the results of these calculations agree well with the independent determinations of the electronegativities of corresponding atoms[173]. The optical determination of the electronegativities of atoms in crystals has been described[56,58,59].

Table 10 gives the system of electronegativities of atoms in crystals, averaged from the results of various methods.

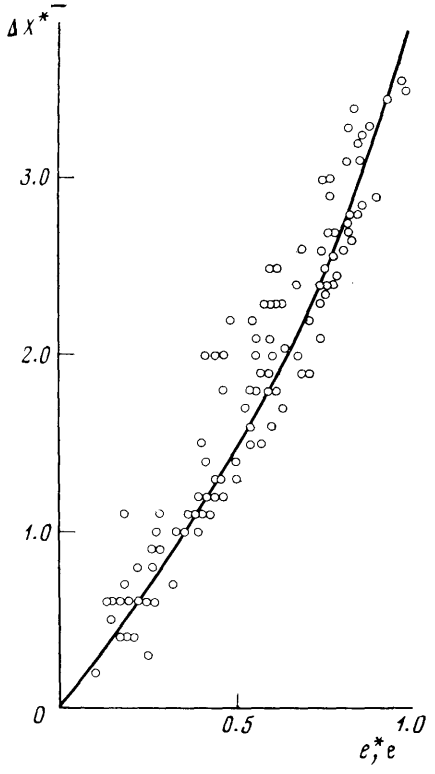


Figure 1. Variation of the effective charges of the atoms according to Szigeti with the differences of the electronegativities of atoms in crystals.

Table 10. System of electronegativities of atoms in crystals.

Period	1A	2A	3A	4A	5A	6A	7A	8A	1B	2B	3B	4B	5B	6B	7B
II	Li 0.6	Be 1.1									B 1.7	C 2.4	N 2.8	O 3.2	F 3.9
III	Na 0.5	Mg 0.9									Al 1.4	Si 1.6	P 2.0	S 2.4	Cl 3.2
IV	K 0.4_5	Ca 0.7	Sc 1.0	Ti 1.2	V (II) 1.2 (III) 1.5	Cr (II) 1.2 (III) 1.4 (IV) 1.6	Mn (II) 1.2 (III) 1.3 (IV) 1.5	Fe (II) 1.2 (III) 1.4	Co 1.2 1.4	Ni 1.2 1.4	Cu (I) 1.0 (II) 1.4	Zn 1.2	Ga 1.4	Ge 1.7	As 1.8	Se 2.3	Br 3.0
V	Rb 0.4	Sr 0.6_5	Y 0.9	Zr 1.1	Nb (III) 1.2 (V) 1.5	Mo (III) 1.2 (IV) 1.4	Tc (IV) 1.4	Ru (II) 1.3 (IV) 1.5	Rh 1.4 1.6	Pd 1.4 1.6	Ag 1.0	Cd 1.1	In 1.4	Sn (II) 1.4 (IV) 1.7	Sb (III) 1.5 (V) 2.0	Te 2.2	I 2.8
VI	Cs 0.3_5	Ba 0.6	La* 0.9	Hf 1.1	Ta (III) 1.1 (IV) 1.5	W (III) 1.2 (IV) 1.4	Re (IV) 1.5	Os (II) 1.3 (IV) 1.6	Ir 1.4 1.6	Pt 1.5 1.7	Au (I) 1.1 (III) 1.7	Hg 1.3	Tl (I) 1.1 (III) 1.5	Pb (II) 1.3 (IV) 1.8	Bi (III) 1.4 (V) 2.0	Po 2.0	At 2.4
VII	Fr 0.3	Ra 0.5_5	Ac 0.8												
	Actinides			Th (IV) 0.9	Pa (IV) 0.9 (V) 1.3	U (IV) 1.0 (V) 1.4 (VI) 1.7									

* $X_{Ln(II)} = 0.8$; $X_{Ln(IV)} = 1.0$.

On constructing graphs of the effective charges of atoms in crystalline compounds (Tables 5 and 6) against the difference in the electronegativities of the corresponding atoms (Fig.1), then the best curve obtained by the least squares method, can be used to find the function $i_{cr}(\Delta X)$, which allows the effective charges of atoms in crystals to be estimated. Table 11 gives the numerical values of the bond ionicities in the molecules, from formula (10), and in crystals as a function of ΔX.

The discrepancy between the experimental and calculated (Tables 10 and 11) effective charges of the atoms averages ±0.05 e or 10% of the absolute value of e^*. The exceptions are certain compounds of the B subgroups, for example, Cu, Ag, and Tl.

Table 11. Variation of the bond ionicity (%) with the difference in the electronegativities of the atoms.

ΔX	i_{mol}	i_{cr}	ΔX	i_{mol}	i_{cr}	ΔX	i_{mol}	i_{cr}	ΔX	i_{mol}	i_{cr}
0.1	1	4	1.0	20	36	2.0	51	64	3.0	80	85
0.2	2	8	1.2	26	42	2.2	58	69	3.2	84	88
0.4	5	16	1.4	32	48	2.4	64	73	3.4	88	91
0.6	9	23	1.6	38	54	2.6	70	77	3.6	91	94
0.8	14	29	1.8	44	59	2.8	75	81	3.8	93	97

The question of the reasons for this exception were recently considered by the example of compounds of the AB type[174]. The widely held opinion that the bonds for compounds of the B subgroup metals are more covalent than those for the compounds of the corresponding analogues in the A subgroups is based on the peculiarities of the geometric structure, the significantly different atomisation energies and melting points, the solubilities of the corresponding salts in water, and other physicochemical properties. In addition, the effective charges of the atoms determined by Eqn.(14) for Cu, Ag, Tl, and Pb halides are higher than for their analogues from the A subgroups. In the first stages of the development of the Szigeti method this circumstance even cast doubt on the legitimacy of the approach itself. However attention was subsequently paid to the following circumstance.

When valency is treated in the classical approach as the number of electrons provided by a given atom for the formation of chemical bonds, then can Cu be regarded as univalent in CuCl, and Pb as bivalent in $PbBr_2$? In fact, the energy of atomisation of univalent metals of the A subgroup K, Rb, and Cs are 21.3, 19.3, and 18.2 kcal $mole^{-1}$ respectively, whereas their analogues in the B subgroup Cu, Ag, and Au have energies of 80.7, 68.1, and 88.2 kcal $mole^{-1}$ respectively[175]. This difference is due to additional metal–metal bonds, which are formed by the atoms of elements of the copper subgroup in the solid state. According to Pauling[23], these elements in the pure metallic state have effective valencies (owing to the use of the *d*-electrons of the preceding layer), equal to $\nu^* = 5.6$. Coulson[141] in comparing the atoms Na and Cu, notes that the 3d-orbitals of neighbouring Cu atoms are overlapped much more strongly than the 2*p*-orbitals of the Na atoms. Therefore for copper it is impossible to think that bonds are formed exclusively with the aid of 4*s*-electrons. On taking into account the features of the zone structure of the copper and silver halides other investigators[83,176] took the effective valency of Cu and Ag to be 1.5. The valency (z) is in the denominator of Eqn.(14) and on dividing the experimentally determined effective charges in the copper and silver polyhalides by 1.5, this leads to an approach between the experimental and calculated values of the bond ionicities in these compounds. An X-ray spectroscopic investigation[177] confirmed the theoretical estimates.

The problem of the increased formal valency due to the participation of the lone electron pairs in the chemical bonds was investigated in the lead dihalides. As already mentioned, Axe and coworkers[124] were the first to suggest that the 6*s*-electrons of lead participate in the chemical bonds in compounds of the $PbHal_2$ type. Investigations of the electron structure of the lead dihalides[178–181] confirmed that the 6*s*-electrons of the Pb atom interact with the *p*-orbitals of the halogen atoms, and only on allowing for this interaction do the calculated bond polarities agree with those determined experimentally.

The above results of the theoretical and experimental investigations pose the important question of what is the real valency of the atoms in crystalline compounds and whether in the interpretation of physicochemical parameters we are restricted to only the formal valencies. A possible way of settling this question could be the comparison of the effective charges of atoms in crystals determined experimentally by the Szigeti method and estimated theoretically, for example, by the electronegativity method. A marked discrepancy between the results from these approaches will show the necessity of allowing for additional interactions of the atoms.

In the papers cited above[174] in addition to Cu, Ag, and Tl halides the chalcogenides of the metals of the zinc subgroup and the compounds of Ga and In with the group V elements are also considered. The mean effective valencies of the metals of subgroups IB–IIIB in compounds of AB type are 1.5, 2.4, and 3.1 respectively; that is, they increase with participation of the $(n-1)d$-electrons in comparison with the formal valency. The simple division of the effective charges of the atoms of the corresponding elements in crystalline compounds (listed in Table 5) by these quantities greatly improves the agreement between the experimental results and those calculated by the electronegativity method.

VI. THE PHILLIPS–VAN VECHTEN ZONE THEORY, BOND IONICITY AND THE STRUCTURE OF CRYSTALS

The Szigeti method gives good results in studying the nature of chemical bonds in dielectrics—ionic-covalent crystals. Essentially, it is based on the assumption of the total localisation of the valence electrons on the atom-partners of the chemical bond and does not take into account the possibility of the appearance of even a partly metallic character at the chemical bond of a crystalline compound.

The approach described in the present section, on the other hand, is based on the assumption that all the valence (outer) electrons of atoms in crystals are delocalised just as happens in metals and the laws of an electronic gas are applicable to them. In accordance with the Penn theory[182]:

$$n^2 = 1 + (h\nu_p/E_g)^2 , \qquad (26)$$

where E_g is the distance between the centres of the valence zone and the conductivity zone (Fig.2), and ν_p the plasma frequency of the vibrations of the valence electrons:

$$\nu_p = (4\pi e^2 N/mV)^{1/2} . \qquad (27)$$

Here N is the number of valence electrons, m their mass, and V the volume of the formula unit of the crystal.

Phillips[42,183–188] and van Vechten[186,187,189] developed, on the basis of these relations, the "dielectric theory of a chemical bond". On writing Eqn.(28) for such elements as diamond and silicon, then for them

$$\varepsilon = n^2 \quad \text{and} \quad E_g = E_{gc},$$

where the index "c" denotes a covalent crystal:

$$\varepsilon = 1 + (h\nu_p/E_{gc})^2 \ . \qquad (28)$$

On assuming that Eqn.(28) is valid for all crystals and that the value of E_g is made up of ionic (E_{gi}) and covalent (E_{gc}) terms, Phillips deduced the equation:

$$E_g^2 = E_{gc}^2 + E_{gi}^2 \ . \qquad (29)$$

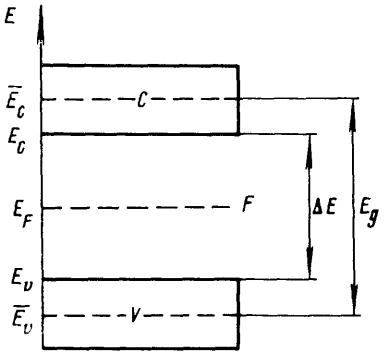


Figure 2. Schematic representation of the zone structure of crystals according to Phillips: V and C are the valence zone and conductivity zone, ΔE is the band gap, E_g the mean energy of transition of the valence electrons into the conductivity zone, and F the Fermi level.

It should be noted that before Phillips the papers of Suchet[190] and Batsanov[191] had already calculated the width of the zone gap of semiconductors from ionic and covalent components; however, Phillips approach is better based physically, which provided a possibility of obtaining fundamental results.

Since the use of Eqns.(26) and (28) led to values in good agreement with experiment, it became possible to determine E_{gi} on the basis of relation (29). Analysis of values of E_{gi} obtained empirically established that these characteristics can be presented as functions of the charges and radii of the atoms:

$$E_{gi}(\mathrm{AB}) = 1.5\left(\frac{z_A e^2}{r_A} - \frac{z_B e^2}{r_B}\right) e^{-k_S r} \ , \qquad (30)$$

where z_A and z_B are the valencies and r_A and r_B the radii of atoms A and B, $r = \frac{1}{2}(r_A + r_B)$, and k_S is the Thomas–Fermi screening factor. The last term ($e^{-k_S r}$) signifies that the valence electrons in a semiconducting crystal are considered to be free (as in metals) and therefore Thomas–Fermi statistics are completely applicable to them.

Expression (30) provided Phillips[188] with a basis for calculating the electronegativities of atoms by the formula:

$$X = 4.0\,(z/r)\,e^{-k_S r} + 0.5 \ , \qquad (31)$$

in which the coefficients 4.0 and 0.5 were chosen so that the Pauling scale was satisfied for the elements C and N. The results of the calculations by formula (31) have been published[47,192,193].

According to Phillips, the bond ionicity in a crystal is determined on the basis of Eqn.(29) by the formula:

$$f_i = E_{gi}^2/E_g^2 \ . \qquad (32)$$

Results of calculations by this formula are given in Tables 12 and 13.

Table 12. Bond ionicity (%) in crystals of type AB (according to Phillips).

A (I)	B (I)			
	F	Cl	Br	I
Li	91	90	90	89
Na	95	94	93	93
K	95	95	95	95
Rb	96	96	96	95
Cs	—	96	96	96
Cu	—	88	88	86
Ag	—	96	93	90
Tl	94	94	94	93
A (II)	**B (II)**			
	O	S	Se	Te
Be	62	61	61	59
Mg	84	79	79	59
Ca	92	91	90	90
Sr	93	92	92	91
Ba	93	93	94	94
Zn	65	62	62	60
Cd	78	68	68	67
Hg	—	70	5	5
Ge [197]	—	—	68	52
Sn [198]	84	76	72	64
Pb [198]	86	79	76	65
Mn	89	78	68 *	55 *
A (III)	**B (III)**			
	N	P	As	Sb
B	26	6	3	
Al	44	39	43	43
Ga	45	33	31	26
In	50	42	36	33

Kolmykov[194] carried out an interesting transformation of the Phillips equations. On taking the unity over to the left-hand side of each equation (26) and (28), and then dividing one equation by the other, we obtain:

$$\frac{n^2 - 1}{\varepsilon - 1} = \frac{E_{gc}^2}{E_g^2} = f_c \ , \qquad (33)$$

where

$$f_c = 1 - f_i.$$

Hence

$$f_i = \frac{\varepsilon - n^2}{\varepsilon - 1} \ . \qquad (34)$$

Calculation by Eqn.(34) is the simplest method of calculating the bond ionicity according to Phillips.

In the initial Phillips–van Vechten theory the value of f_i was calculated for crystals of the ZnS and NaCl structure types consisting of sp-elements. Subsequently, the theory was extended to crystals of other structure types and to d-elements. A significant contribution to the dielectric theory was made by Levin[195,196] who in calculating the number of valence ("plasma") electrons for the B subgroup elements took into account all $(n-1)d$-electrons, and not only the ns- and np-electrons. This interpretation is similar to that used in calculating the effective charges of the atoms

of the *d*-elements according to Szigeti. Levin demonstrated very convincingly the correctness of this approach for the example of Cu_2O, where in allowing for only the 4*s*-electron of copper $f_i \cong 0$ is obtained and only when all the 3*d*-electrons are included in the number of plasma electrons was $f_i = 0.56$ e obtained.

Tables 12 and 13 give the Phillips bond ionicities obtained by Levin and also those we have calculated by Eqn.(34) (the latter values are marked by an asterisk).

Table 13. Bond ionicity (%) in crystals of type A_nB_m (according to Phillips).

AB_2	f_i	AB_3	f_i	A_2B_3	f_i
MgF_2	91	SiO_2	57	Al_2O_3	80
CaF_2	97	Ge^4O_2	51	Cr_2O_3	78
SrF_2	97	Ge^6O_2	73	Fe_2O_3	68
BaF_2	97	SnO_2	75*	As_2S_3	29*
ZnF_2	89	SnS_2	49*	As_2Se_3	28*
CdF_2	93	$SnSe_2$	44*		
$CdCl_2$	66*	TiO_2	94*		
$CdBr_2$	68*	TiS_2	84*		
CdI_2	68*	$TiSe_2$	69*		
PbF_2	94	ZrS_2	75*		
PbI_2	80	HfS_2	76*		
		$HfSe_2$	81*		

Comparison of the results in Tables 12 and 13 and Tables 5 and 6 shows that the bond ionicities determined by the Szigeti and the Phillips methods are not the same. The physical reason for the differences was discussed above and we will now consider the interconnection between i (Pauling–Szigeti method) and f_i (Phillips method).

Lawaetz[176] found that

$$e^*/z \sim E_{gi}/h\nu_p.$$

Hence by using Eqn.(26) Uemil[192] obtained the expression:

$$(e^*/z)^2 \sim f_i/(n^2-1) \quad . \tag{35}$$

The physical significance of this relation is completely understandable, since the charges according to Szigeti are identical to the Pauling bond ionicity and the latter, according to Eqn.(11), is determined by the energies, whereas the charges according to Phillips depend on the square of the energy—cf. also the exponent of the powers of $(\varepsilon - n^2)$ in Eqns.(14) and (34).

The Phillips–van Vechten theory was modified in several subsequent studies. Thus Unger and Neumann[200] found that

$$f_i = \frac{1}{2}\left(1 - \cos\pi\frac{E_{as}}{E_{vb}}\right) \tag{36}$$

where E_{as} is the antisymmetric energy gap [within the valence band (Ed. of Translation)] and E_{vb} the total valence band width of the crystal. Later the same formula was used by Hübner[201,202] for calculating the bond ionicities in a series of transition metal oxides and halides.

Hübner also considered the application of the Phillips–van Vechten method to amorphous materials. Since according to Phillips

$$E_{gi} \backsimeq r^{-1}, \quad E_{gc} \backsimeq r^{-2.5} \tag{37}$$

it is easy to see that

$$\begin{aligned} E_{gc}^2(\text{am}) &= E_{gc}^2(\text{cr})\,(\rho_{\text{am}}/\rho_{\text{cr}})^{5/3}, \\ E_{gi}^2(\text{am}) &= E_{gi}^2(\text{cr})\,(\rho_{\text{am}}/\rho_{\text{cr}})^{2/3}, \\ \nu_p^2(\text{am}) &= \nu_p^2(\text{cr})\,(\rho_{\text{am}}/\rho_{\text{cr}}) \end{aligned} \tag{38}$$

where ρ_{am} and ρ_{cr} are the densities of the amorphous and crystalline phases. The dielectric constants of amorphous substances calculated by these formulae agree satisfactorily with experiment.

Hübner[203] investigated in special detail the bond ionicity in various forms of SiO_2 crystals. He found that the refractive index of silicon dioxide obeys the equation:

$$n = 1.04 + 0.19\,\rho,$$

where ρ is the density of various modifications of SiO_2. On taking into account that $\nu_\rho \cong \rho$, we obtain:

$$n = [1 + (n_\alpha^2 - 1)\,\rho/\rho_\alpha]^{1/2} \tag{39}$$

where the subscript α denotes α-quartz. Later, Hübner obtained the formula:

$$n^2 = 1 + 1.26r^2(1 - f_i) \tag{40}$$

where r is the minimal Si–O distance in the corresponding structure. Hence the following values are obtained for f_i: α-quartz 0.57; β-quartz 0.60; α-tridymite 0.59; α-cristobalite 0.58; β-cristobalite 0.61; coesite 0.53; keatite 0.59; glass 0.65.

A new variant of the Phillips formula was proposed[204]:

$$f_i = V_a^2/(V_s^2 + V_a^2), \tag{41}$$

where V_a and V_s are antisymmetric and symmetric form-factors of the potential of the crystal which are determined from the value of E_g. Comparison of the results obtained by Eqn.(41) with Phillips' results shows their agreement.

In conclusion, we note that the Phillips–van Vechten theory went firmly into the arsenal of the methods of solid-state quantum chemistry and physics, and it is now difficult to list all the studies where the dielectric theory of the chemical bond is used or developed. The present review surveys only the main works on this method of studying the chemical bond in crystals. Additional information can be obtained elsewhere[192,196,205–207].

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Having considered the history and contemporary state of the use of dielectric methods in studying the nature of the chemical bond in chemical substances in any state of aggregation, it is easy to be persuaded that the information obtained with this method is in complete agreement with structural theory and with the results of independent methods of investigating bond polarities. The relative simplicity and rapidity of the measurements, together with their universality and low requirements for the quality of the test specimens makes this method extremely attractive for chemists.

For the future, the most interesting problem is the study of changes in the nature of the chemical bond at high pressures (up to the transformation of a dielectric into the metallic state).

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The Possibility of Predicting the Retention Parameters in Gas-Liquid Chromatography

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Various methods for the calculation of retention parameters used in gas-liquid chromatography are critically examined in this review. They have been divided into four groups in accordance with their fundamental postulates. Attention has been concentrated on the physicochemical foundations of the methods considered, their generality, and the errors of the calculated quantities. The bibliography includes 325 references.

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INTRODUCTION

Like any other analytical method, analytical gas–liquid chromatography (GLC) involves qualitative and quantitative analyses. The physical detection methods and the fairly simple calculations from output data made it possible to solve, in the main, the problems of quantitative analysis. However, the problems of qualitative analysis have not so far been fully solved. The situation can be accounted for by the unsatisfactory level of development of the theory of solutions, which is mainly concerned with the concentration dependence of the solubility of spherical molecules[1,2] rather than by the deficiencies of the gas-chromatographic method. The experimental data on the properties of infinitely dilute non-electrolyte solutions, one of the components of which is highly volatile and the other is involatile, have become available only after the introduction of the GLC method and have not so far been examined with the theory of solutions.

The practice of qualitative analysis in GLC requires the creation of fairly simple and universal methods for the *a priori* calculation of the retention parameters of the substances to be separated (sorbates); such calculation is essential despite the availability of a fairly large number of auxiliary identification methods in GLC.[3] This is because each identification method yields an answer with some degree of uncertainty, which diminishes when data obtained by another, independent method, are resorted to.

Although more than 400 communications describing various methods for the *a priori* calculation of retention parameters in GLC have been published, their results have not so far been surveyed. The aim of the present review is to examine the *a priori* and correlation methods for the calculation of retention parameters in GLC and to discuss their physicochemical basis.

The physicochemical picture of retention in GLC is fairly complex[4] and is determined not only by solubility (liquid–gas equilibrium) but also by a number of adsorption processes at the interfaces. For a more unambiguous treatment of retention parameters, we shall examine below mainly systems where adsorption processes play a negligible role (non-polar systems or systems with low polarity). The questions of complex formation via hydrogen bonding are outside the framework of this review; its limited size also precludes the consideration of the influence of changes in the nature of the stationary phase on retention parameters. The data described are grouped in terms of the methodological principles of the approach to the calculation of retention parameters.

II. THE USE OF THE PRINCIPLE OF THE ADDITIVITY OF THE INCREMENTS IN THE MOLAR FREE ENERGY OF SOLUTION

The molar free energy of the gas–liquid phase transition ΔG_S (in the chromatographic literature it is usually referred to as the molar free energy of solution) is related to the gas–liquid partition coefficient K by the expression

$$\Delta G_S = -RT \ln K = -RT \ln V_N, \quad (1)$$

where V_N is the pure retention volume. The idea of employing the additivity of the molar free energy of solution in terms of groups of atoms in the sorbate molecule for the calculation of retention parameters is extremely attractive[5,6], although it is based solely on phenomenological observations[7]. A test of the applicability of this additivity principle to gas-chromatographic systems has been described in detail[7-13].

For monofunctional aliphatic compounds, it is possible to formulate an equation involving the number of methylene (n_{CH_2}) and methyl (n_{CH_3}) groups in the sorbate molecule and the energy F of the interaction of the atomic group with the stationary phase (the subscripts x, CH_2, and CH_3 denote the parameters of the functional group investigated and the methylene and methyl groups respectively):

$$\ln V_N = F_{CH_3} n_{CH_3} + F_{CH_2} n_{CH_2} + F_x. \quad (2)$$

The total number of carbon atoms in the sorbate molecule $n = n_{CH_3} + n_{CH_2}$. For $n > 5$, the last equation can be fitted by a linear relation of the type[14-16]:

$$\ln V_N = F_{CH_2} n_{CH_2} + F_x. \quad (3)$$

Eqn.(3) is used most widely in practical qualitative analysis in GLC although the error of the correlations in terms of the corresponding variables has been estimated in only a small number of publications[17-19]. In precise measurements of retention parameters, it was found that, even for the homologous series of n-paraffins in non-polar or weakly polar stationary phases, Eqn.(3) does not hold, and particularly marked deviations are observed in the case of stationary phases whose molecules contain cyclic groups of atoms[20-24]. However, despite the reliable data presented in the studies quoted above, reports are being published from time to time claiming a satisfactory linear relation between $\ln V_N$ and n (see, for example, the report of Wainwright et al.[25], who do not even indicate the errors of the calculated data and whose method of calculating the dead retention volume does not appear trustworthy).

Numerous publications have shown[26-29] that the slopes of the relations between $\ln V_N$ and n are not the same for different homologous series. In the presence of polar functional groups, both in the sorbate molecule and in the molecule of the stationary phase, the relation between $\ln V_N$ and n becomes non-linear[26,30]. Even when non-polar and weakly polar sorbates and stationary phases are used, the errors of calculations by Eqn.(3) for homologous series of sorbates are at least 3% [31] and the linearity of the relation between $\ln V_N$ and n holds only for a comparatively small number of members of homologous series. For example, the linear relation between I and n (I is the Kovàts retention index proportional to $\ln V_N$) holds only for two–three neighbouring homologues in the series of phenols [on a column with poly(phenylether)] and for the series of phenols, it is not even possible to find linear sections[32]. Some investigators[33] suggest that an empirical correction factor be introduced to correct the non-linearity of the relation between I and n, which converts Eqn.(3) into a semiparametric equation. When the methylsilicone elastomer OV-1 is used, the correlation coefficient for different homologous series varies in the range from 0.97 to 0.98, which is unacceptable for chromatographic measurements.

The number of carbon atoms in the sorbate molecule is by no means the only parameter which can be used to construct linear relations between the free energy of solution and the chemical composition of the molecule; attempts to set up correlations between $\ln V_N$ and I and the number of silicon[34], sulphur[35], nitrogen, and oxygen[36] atoms, phenyl groups[37], double bonds[38,39], and homogeneous *cis–trans* configurations[17,40] in sorbate molecules have been described. Parameters such as the equivalent chain length *Me*,[41,42] the steroid number R_{Mg} in the series of steroids[43,44], and the equivalent length of the carbon chain in the case of unsaturated aliphatic esters[45-48] have an analogous significance.

Eqn.(3) is not used solely for the interpolation or extrapolation of retention data for a selected homologous series; it also makes it possible to estimate the contribution of functional groups to the molar free energy of the interaction of the sorbate with the stationary phase. Thus the increments in $\ln V_N$ for a large number of functional groups (H, CH_3, C_2H_5, F, Cl, Br, I, OCH_3, CN, NO_2) in anilines, phenols, pyridines, aromatic hydrocarbons, cyclohexanes, and hexanes have been determined with the aid of an equation of type (3) using Carbowax 20M and Apiezon L as stationary phases[49].

In general, a functional group can be understood not only as a group containing heteroatoms but as any structural group distinguished both by the presence of multiple or aromatic bonds and by a non-linear arrangement of carbon atoms in space. In particular, for hydrocarbons, the presence of such structural groups in the molecule can be the cause of a change in the retention of the sorbate. In order to take into account the influence of individual structural groups as well as groups of carbon atoms linked by multiple bonds on the free energy of solution, it has been suggested[50] that the homomorphous factor H be calculated:

$$H = I_x - I_h, \qquad (4)$$

where the subscript h refers to a homomorphous paraffin, i.e. to a saturated hydrocarbon having the same carbon skeleton as the compound investigated.

The principal information obtained with the aid of Eqn.(4) characterises the influence of multiple bonds on retention parameters. The values of H have been determined in a number of studies[50-59] for non-polar and weakly polar stationary phases. On the other hand, similar measurements can be carried out also for polar sorbates, for example for alkylchlorosilanes[60] on weakly polar silicone stationary phases (PMS-100, E-301, SE-30, and DC-550); however, in such systems account must be taken of the length of the alkyl group in the member of the homologous series (the relation between I and n is non-linear). Since the considerations arising in the determination of the homomorphous factor H do not differ fundamentally from those used to determine F_X, the errors in the calculation of H by Eqn.(4) are also of the same order of magnitude. For example, the relative standard error $s°$ is in the range 2–5% for aromatic hydrocarbons, alkyl sulphides, and ketones[61]. The contributions of aliphatic isoalkyl and unsaturated groups of atoms as well as sulphur atoms in metameric thiatridecanes have been determined[62].

Since the fundamental non-linearity of the relation between $\ln V_N$ and n has been demonstrated in numerous studies, a series of approaches have been devised, using specific mathematical modifications of Eqn.(3) to reconcile the calculated and experimental data with the aid of empirical parameters. For example, the following relation has been obtained in a series of studies by Golovnya and coworkers[62-69]:

$$I = k_1 + k_2 n + k_3/n, \qquad (5)$$

where k represent constants. It has been used to interpret retention data for n-alkyl sulphides[63], n-alkyl isoalkyl sulphides[64], alkyl vinyl, alkyl allyl, and alkyl propyl sulphides[65], thiophen, furan, and benzene derivatives[66], aliphatic di-isoalkyl sulphides[67], heterocyclic compounds[68], and di- tri-, and tetra-sulphides with an S–S bond[69] on four stationary phases (Apiezon M, silicone OV-17, Triton X-305, and PEG-1000).

The relevant considerations do not change fundamentally if the increments of the free energy of solution of the atomic groups of the sorbate are replaced by bond increments[70,71]. The assumption of the additivity of the values of ΔG_s for different bonds leads to the same computational errors as the hypothesis that the ΔG_s are additive with respect to atomic groups[72-75]. An attempt to take into account the influence of neighbouring bonds on the retention parameter for a selected bond has been made in a study[76] where the so-called bonding indices χ were used. However, in order to obtain linear relations, it was necessary to introduce a series of empirical parameters (for example, the distance A between the neighbouring bonds or methyl groups):

$$I = 200(\chi - 1.4142) + 100 + A^2. \qquad (6)$$

This equation has been used to calculate the retention parameters of isoalkanes[76]. The influence of neighbouring bonds and substituents on the increments in I for individual functional groups has been determined in a study[77] where mono- and di-alkylbenzenes were separated on squalane, Yukon LB-550X, and Yukon HB-280X at 100 °C; the average standard error of the calculation s was six retention index units.

The principle of additivity underlying Eqn.(3) is applicable primarily to monofunctional homologous series. When polyfunctional sorbates are considered, the additivity of the contributions of the functional groups to the molar free energy of solution holds only for substances where the functional groups are separated by a linear carbon chain consisting of at least three carbon atoms. In other cases account must be taken of the mutual influence of the carbon groups, which is expressed by the so-called second-order increments[54,55,59]. The magnitude of these corrections is so great that they cannot be neglected: for example, for paraffins with molecules containing three and four methyl side groups, they amount to 30 and 40 Kováts index units† respectively[76]. The second-order corrections are particularly large for very polar sorbates: thus for alcohols they vary in the range from 170 to 270 units. However, when weakly polar stationary phases such as methylpolysiloxanes or phenylmethylsiloxanes of the PPMS type are used, even the introduction of corrections of this kind does not reduce the errors of the calculation for polyfunctional sorbates below 4% and for a more polar stationary phase (SKTFT-50X) the error increases to 10%.

The non-additivity of the values of I in a homologous series is indicated by data presented in numerous publications. Thus, for the homologous series of isoparaffins on a series of stationary phases [tetracosane, squalane, dotriacontane, di(4-isopropylbenzyl)benzene and its analogues], the quantity I varies from 56 to 64 units[77], whereas the value required by theory is 100 units. According to the results of the same study[77], the increment in the retention index for alkylbenzenes varies from 102 to 95 for the homologous series investigated. Similar variations have been noted for n-alkynes on stationary phases of low polarity and, when polar stationary phases are used, the corresponding increments are in the range between 84 and 94 units.[78,79] The increment in the retention index in the homologous series is 90–95 units for dibasic acid esters[80], 50–125 units for alkylbiphenyls[81], 75–105 [82] and 60–100 units[83] for alkylbenzenes on three stationary phases of different polarity, and between 94 and 100 units for olefins[84].

Such phenomena indicate the need to seek more complex mathematical relations for the calculation of experimental retention parameters. Thus an equation of the type

$$I = k_1 + k_2 n + k_3 n^2 \qquad (7)$$

has been used[79] to calculate the retention indices of n-alkynes on a highly polar stationary phase—1,2,3-tris(2-cyanoethoxy)propane. However, no account was taken in the above study[79] of adsorption at the gas–liquid interface.

The data presented indicate a low accuracy of the calculation of retention parameters in homologous series using only one variable parameter—the number of carbon atoms in the molecule. Fairly large errors have also been observed after the introduction of second-order corrections taking into account the immediate environment of the functional groups. These failures are readily explicable in the analysis of the physicochemical basis of the relations employed. The molar free energy consists of two components: the molar heat of solution ΔH_S and the molar entropy of solution ΔS_S. If ΔH_S is treated to a first approximation as a quantity additive with respect to the atomic groups of the molecule, then ΔS_S is determined by the relative positions of the atomic groups rather than by their complete set. The greater the contribution of the entropy factor to the molar free energy of solution, the less applicable the principle of additivity to the description for the behaviour of the molar free energy of solution, i.e. to the calculation of $\ln V_N$ and I.

Despite the lack of a physicochemical basis, the principle of additivity is so simple and attractive that attempts to use it in the calculation of retention parameters have continued—mainly by increasing the number of empirical and semi-empirical parameters in the overall equation. Thus a multiparametric equation has been used[85] to describe the retention of diphenyl ether derivatives on weakly polar stationary phases. A three-parameter equation has been used[86] to describe the retention of aromatic ethers and their fluoroderivatives (taking into account the relative positions of the substituents).

One of the most fruitful approaches in the empirical calculation of retention in GLC involved the use of the principles of topological analysis[87,88]. According to this method, one must take into account the immediate environment of a given functional group–the first, second, third, etc. spheres. The reliability and accuracy of the calculation increase with increase in the number of surrounding spheres taken into account but at the same time there is also a sharp increase of the number of empirical parameters to be determined beforehand for the calculation, which requires in its turn the accumulation of extensive experimental data for the retention of the test compounds. Thus, in the calculation of the retention of alkanes with allowance for the influence of the first sphere of the environment, use is made of 14 parameters, while in the calculation with allowance for the influence of the second sphere the number of such parameters increases to 2000.[7] At the same time it has been shown that[7], even when 90 empirical parameters are used for C_4–C_8 olefins, the average standard deviation of the calculated data from experimental results is 11%.[7] The principles of the topological calculation of the retention indices of isoalkanes have been discussed[89]; the same method has been used[10] to calculate the retention parameters of 84 linear alkenes (up to tetradecane) on squalane using 25 empirical parameters. The average standard deviation of the calculated results from the experimental data is 3–4 units.

As a rule, in the topological analysis of experimental data and in the derivation of computational equations, computers are widely used because of the large number of calculations. For example, the DARC programme has been used in a series of investigations[87,91–93]; in calculations by means of this programme with 18 empirical topological constants, the average standard deviation from the experimental data for C_6–C_8 isoalkanes is 3.1 units[94] (one should bear in mind that the experimental data for 50 hydrocarbons must be used to calculate 17 topological parameters). With increase of the number of the empirical topological parameters to 23, the average standard deviation decreases by a factor of two. However, errors of such magnitude are characteristic solely of interpolation calculations; in the extrapolation of data the errors usually increase several times. The application of other computer programs leads to errors of the same order of magnitude[95–98].

Despite the considerable number of experimentally determined parameters for calculations in accordance with the topological scheme, the final result depends in many respects on the intuition of the investigator, who must choose correctly the test substances[76]. In order to increase the accuracy of the calculations and to reduce the required number of empirical parameters, the treatment has been restricted in certain studies to isotopological series of compounds, which reduces the error of the calculation almost by a factor of two[94]. Another (similar) characteristic of the sorbates—the degree of bonding—has been used also to calculate retention parameters[99]. The bonding indices have been employed to calculate the retention of polycyclic aromatic hydrocarbons[100],

† Henceforth for brevity the expression "Kováts index units" will be replaced by "units".

alcohols, ketones, and ethers on polar stationary phases[100] and of hydrocarbons, ethers, carbonyl compounds, and alcohols[102] on weakly polar stationary phases. It has been shown[102] that, whereas the employment of bonding indices for hydrocarbons has resulted in an error of calculation less than one unit, for oxygen-containing compounds the error is much greater (between 5 and 190 units). The errors can be reduced only by employing multiparametric equations.

The data described above permit certain conclusions. The principle of the additivity of the molar free energy of solution (for the determination of I, $\ln V_N$, and $\ln K$) does not hold even for members of a homologous series and can be used only for a preliminary estimation of the order of magnitude of the yields of the test components. The contribution of each functional group to the molar free energy of solution depends to a large extent on the influence of the neighbouring groups of atoms, which makes it necessary to resort to methods of topological analysis for a complete quantitative estimation of the interaction energy. The method of topological analysis as well as multiparametric equations with empirical constants can ensure a comparatively low error of the calculation (approximately 5–10 units), but such methods require a large number of preliminary experimental data. The greater the number of empirical constants used in the calculation, the greater the accuracy. The value of the data obtained by this approach is also reduced by the fact that they are of the interpolation type, the errors increasing appreciably on extrapolation of the equations to higher homologues. Consequently the methods employing the principle of additivity can be regarded only as a first approximation in the calculation of retention data and also as a convenient method of an abbreviated formulation of experimental information for homologous and isotopological series of sorbates.

III. CORRELATION BETWEEN THE RETENTION PARAMETERS AND THE PHYSICOCHEMICAL PROPERTIES OF SORBATES

Purely empirical methods based on the principle of additivity for the calculation of the retention characteristics require preliminary experimental studies if sufficiently accurate results are to be obtained. It is useful to attempt to diminish the set of predetermined parameters by introducing into the equations parameters related to the physicochemical properties of the substances to be separated. The retention parameters are related to the properties of the sorbates and of the stationary phase and their simplest correlations with the properties of sorbates merit particular attention.

The boiling point of the sorbate T_b is the characteristic most widely used for correlations, because it is one of the most readily available. The following relation has been postulated in a series of studies[103–109]:

$$\ln V_N = k_1 + k_2 T_b \ . \qquad (8)$$

Indeed the relative retention volume r can be expressed in terms of V_N and the activity coefficient γ:

$$r = V_{N_1}/V_{N_2} = \gamma_1 p_2^0/\gamma_2 p_1^0 \qquad (9)$$

where p^0 is the vapour pressure of the pure sorbate. Then

$$\ln r = \ln(\gamma_1/\gamma_2) + \ln(p_2^0/p_1^0) \ . \qquad (10)$$

According to Trouton's rule (a not altogether correct approximation), the molar entropy of evaporation ΔS_v at the boiling point of a given substance is constant, whereupon

$$RT \ln p^0 = k_3 - \Delta H_v \ , \qquad (11)$$

where ΔH_v is the molar heat of evaporation. Subject to a series of significant stipulations, the molar heat of evaporation can be replaced by the boiling point, which permits a reformulation of Eqn.(11):

$$\ln p^0 = k_4 + k_5 T_b \ . \qquad (12)$$

Finally, if it is assumed that γ_1/γ_2 is constant, we obtain an equation of type (8) linearly relating the boiling point of the sorbate to its retention.

All the assumptions made virtually reduce the applicability of the linear relation between the logarithm of the retention volume and the boiling point of the sorbate to the members of a single homologous series and even here the relation is considerably strained. This is indicated by data obtained for paraffins and olefins on non-polar stationary phases, i.e. for the most ideal solution; for this correlation, $s^0 = 2\%$.[104] The average standard error of the calculation for simple monofunctional compounds based on the linear relation between I and T_b amounts to 5 K when Apiezon L and Carbowax-20M are used as the stationary phases, the error increasing for the lowest members of the homologous series[110]. The relation holds accurately for isomeric hydrocarbons, which actually makes it possible to correct some boiling points of sorbates[111].

The use of the correlation between the boiling points of sorbates and their retentions can be recommended only for non-polar stationary phases. With increase of the polarity of the stationary phase, the correlations become non-linear[109,112,113]. To correct this disadvantage, various correction factors have been proposed. For example, the ratio z of the number of carbon atoms in the aromatic ring to the total number of carbon atoms in the molecule has been employed[113]. The equation derived is applicable to alkylbenzenes with Carbowax-1500 as the stationary phase:

$$I = 6.5T_b + 7.66z - 305 \ . \qquad (13)$$

The average standard deviation of the data evaluated by this equation for C_7–C_{13} alkylbenzenes is 6.5 units. Particularly large deviations from the linear relation between I and T_b are observed in cases where there is steric hindrance to the interaction: for aromatic hydrocarbons[113–116], phenols[117], and heterocyclic compounds[118]. The claims that the deviations s for correlations of this kind involving a series of different classes of substances, including polar compounds, do not exceed one unit are rendered unreliable by all these factors[119–124].

As stated above, the similarity of the properties leads to a satisfactory correlation between I and T_b for isomeric compounds. The difference between Kováts indices for such compounds ΔI is linearly related to T_b:[125,126]

$$\Delta I = k\Delta T_b \ , \qquad (14)$$

but the proportionality coefficient k varies within wide limits. For example, Kováts and Vehroi[127,128] have found it to be 5, while Gastegnau and Villesot[129] obtained a value of 6.5.

Since the molar heat of evaporation varies somewhat with temperature, it has been suggested[130] that the column temperature T_c be taken into account by the relation

$$\ln V_g = k_1 + k_2 T_b/T_c \qquad (15)$$

where V_g is the specific retention volume. A family of parallel lines have been obtained in terms of the variables of this equation for hydrocarbons on the silicone elastomer E-301 and have been used to identify substances in homologous series[131–133], although more careful studies[134] indicate some curvature in relations of this kind.

The availability of the boiling points of many organic compounds has led to a large number of attempts to employ T_b as a parameter defining retention. For example, the temperature retention index has been proposed[133]. It is related to

the Kovats index in the following manner:

$$(\lg V_{Nx} - \lg V_{Nn})/(\lg V_{N(n+1)} - \lg V_{Nn}) = (T_{bx} - T_{bn})/(T_{b(n+1)} - T_{bn}), \quad (16)$$

where the subscript x refers to the test substance, n to the n-paraffin with n carbon atoms in the molecule, and $n+1$ to the n-paraffin with $n+1$ carbon atoms in the molecule.

By analogy, the following form of the index has been put forward[135]:

$$I_b = 100n + 100(\lg T_{bx} - \lg T_{bn})/(\lg T_{b(n+1)} - \lg T_{bn}) \quad (17)$$

and Shlyakhov et al. proposed yet another formulation[136]:

$$I^0 = (T_{bx} - T_{bn})/(T_{b(n+1)} - T_{bn}) + 100n . \quad (18)$$

The average discrepancy between I and I_ν is 16 units and even on non-polar sorbates such as isoparaffins this quantity is 5.1 units[134], which significantly reduces the value of such indices for practical GLS: however, some workers[135] believe that it is possible to employ the temperature retention index for hydrocarbons.

The molar volume of the sorbate $\overline{V}$ is also used to set up correlations with retention parameters. A linear relation between $\overline{V}$ and $\lg r$ has been established for a non-polar stationary phase[134,135], but, with increase of the polarity of the stationary phase, the correlation between these quantities disappears. A similar correlation has been found for alkynes[136]. The molar volumes of organic compounds are less readily available than the boiling points, which has been one of the main causes of the small popularity of such correlations. Furthermore, correlations of this kind are valid only for a limited number of systems.

The refractive index and the molar refraction characterise the ability of the sorbate to exhibit a dispersion interaction with the stationary phase. Correlations between these quantities and the retention parameters have been found in a number of studies, for example, for acid esters on a silicone stationary phase[137] and for hydrocarbons on phthalate esters[138]. In the latter case the discrepancy between the experimental and calculated data is on average 4 units. Correlations of the same type have been found for dimethylbiphenyls and xylenes[139], perhalogenoalkanes[140], and certain other classes of organic compounds[141,142]. The attempts to establish correlations between the retentions and the parachors of sorbates has been described[143].

It has been shown[143] that $\ln V_N$ is proportional to the quantity $(M - 170)^{1/3}$ for organoarsenic compounds on a silicone stationary phase (M is the molecular weight of the sorbate). By analogy with the Kovats retention indices, a molecular retention index has been proposed[144], using the molecular weights of the test substance and n-paraffins. In the presence of steric hindrance to intermolecular interaction, the correlation between the retention and the molecular weight disappears[145]. However, the molecular weight of the sorbate as well as its refractive index and molar refraction can be correlated solely with the energy of the dispersion interaction and for this reason the application of the above quantities is limited solely to non-polar systems, where the dispersion interaction plays the main role.

The orientational and inductive interactions of the sorbate with the stationary phase can be taken into account by resorting to the dipole moment of the molecule μ (the orientational interaction energy is proportional to the square of the dipole moment of the species). The following equation has been proposed[146,147] for the relation between the retention volume and the dipole moment of the sorbate molecule:

$$\ln V_N = k_1 + k_2\mu . \quad (19)$$

However, the dipole moment enters into this equation with a power exponent of unity, which conflicts with the equation for the orientational interaction energy. A correlation between the retention characteristics and the molecular dipole moment of the sorbate has been found for xylidines[148], although such correlations have not been observed for oxygen-containing compounds[149]. The proportionality of the "polar" component of the retention volume to the square of the molecular dipole moment of the sorbate has been established for mononitro-derivatives of aromatic hydrocarbons[150]; on passing to dinitro-derivatives, the proportionality ceases to hold.

We believe that the use of the dipole moment of the entire molecule in the description of the intermolecular interaction in gas-chromatographic solutions is incorrect, since the orientational interactions in such solutions takes place between bond microdipoles[151]. A correlation between the retention and the dipole moment of the sorbate molecule is therefore hardly general. The same considerations apply also to another correlation parameter—the dielectric constant of the sorbate molecule[152,153]. An attempt to use the dispersion interaction as well as the orientational forces to characterise the retention has been made in a study[154] where the bonding parameter [the term $f(\chi)$] and the dipole moment were introduced into the equation

$$I = f(\chi) + k_1\mu^2 + k_2 . \quad (20)$$

The average discrepancy between the retention parameters calculated by this equation and found experimentally is 5–6 units.

The linear correlation postulated[155] between V_g and the viscosity of the sorbate has been tested for a series of dinitriles in polar stationary phases.

The size and shape of the molecule are taken into account by the Wiener three-parameter equation for the calculation of the Kovats indices of alkylbenzenes[156,157]. This approach is intermediate between the pure empirical calculation from the atomic group increments and the attempts to employ a definite physical parameter of the sorbate molecule.

Apart from the physical parameters of sorbate molecules, chemical characteristics such as the Hammett, Taft, Jaffé, and Palm constants have also been used to establish correlations with retention parameters. The Hammett–Taft constants are related to the ionisation potentials of molecules and are determined empirically from the reactivities of specific functional groups. In particular the Hammett constants characterise the energy of the hydrogen bond with phenols.

A relation was derived[158] for a pair of substituted phenols (subscripts 0 and x), which includes the Hammett constant σ, the constant k_1, and the activity coefficients of the phenol molecule (γ) and of a homomorphous molecule which does not form a hydrogen bond (γ^*):

$$\ln(\gamma_0/\gamma_x) = \ln(\gamma_0^*/\gamma_x^*) + k_1\sigma . \quad (21)$$

It follows from Eqn.(20) that, in order to ensure the linearity of the relation between the activity coefficients and the Hammett constants, the ratio γ_0^*/γ_x^* must be constant, i.e. Eqn.(21) is valid only for an isotopical series. As a rule, this is the case for isomeric compounds where the hydrogen bond energy makes a significant contribution to the overall intermolecular interaction energy. When a polyester stationary phase was used, a linear correlation between $\ln(\gamma_0^*/\gamma_x^*)$ and σ for phenols was observed with a correlation coefficient of 0.89 and an error s^0 of 3%.[158] This correlation coefficient for GLC data is extremely low, which indicates a low suitability of the correlation between the retention characteristics and the chemical constants for *a priori* calculations in GLC. A detailed thermodynamic analysis of the application

of Hammett–Taft contants in chromatographic calculations has been carried out[159-161].

The application of Hammett, Taft, and other constants is to some extent justified when there is a significant contribution of specific interactions (for example, hydrogen bonding) to the overall molecular interaction energy in the gas-chromatographic solution. There is hardly any physicochemical justification for the application of these constants in the calculation of the retention parameters of aromatic hydrocarbons and some of their derivatives. However, numerous attempts to find linear correlations of the type[139,162,170]

$$\ln r = k_1 + k_2\sigma \ , \qquad (22)$$

have in fact been made for such systems.

A more complex equation, containing a series of Hammett constants (σ_1, σ_2, and σ_3) has been proposed[49] for the retention parameters of derivatives of aromatic hydrocarbons on Apiezon L and Carbowax 20M:

$$\Delta\ln V_N = k_1\sigma_1 + k_2\sigma_2 + k_3\sigma_3 \ . \qquad (23)$$

The proportionality constants in this equation are found by regression analysis. The relative average standard deviation of the calculated data from experimental quantities was 1.5% for the system investigated. The comparatively high accuracy of the proposed computational method can be explained by the introduction into the equation of three constants with three proportionality coefficients: even without a physicochemical justification, the use of an empirical three-parameter equation can ensure approximately this accuracy of the calculation.

As already stated above, the application of Hammett type constants for the construction of correlations between the retention characteristics and the physicochemical properties of the sorbate is justified only for systems with a significant specific interaction. For the remaining systems (and these are the majority in GLC), one has to introduce a series of correction factors, including the interaction factor i, the resonance factor $\overline{R}$, and the Taft constant σ_0:[171]

$$\ln r = k_1(\sigma_0 + i\Delta\sigma\overline{R}) + k_2 \ . \qquad (24)$$

A number of studies[172-175], in which the characteristics of the steric hindrance to intermolecular interaction E_j, the contribution of the structural element of the sorbate molecule to the retention index I_i, and the empirical increment of the Kovats index for the selected structural group in the aliphatic compounds I_i^0 were used in the calculations, have been carried out on the application of the Taft constant to the calculation of the retention indices of bifunctional compounds (dihalogenoalkanes, halogenoepoxy-compounds, and ethers):

$$I_i = I_i^0 + k_1\sigma + k_2E_j \ . \qquad (25)$$

Correlations between the retention parameters of alkylbenzenes and the Taft constants have also been found in another study[176]. Correlations have also been established between the retention parameters of tri- and tetra-methylbenzenes and the Jaffé constants[177], between the retention parameters of aromatic hydrocarbons and their ionisation potentials[178,179], and between the retention parameters of a series of sorbates and the Palm constants and the Newman's rule of six[180,181]. The following equation was found to hold in the study of alkylpyridines on Carbowax-400, glycerol, Apiezon L, and dinonyl phthalate with a correlation coefficient of 0.99 and $s = 0.021\ln V_N$:[182]

$$\lg\frac{\gamma_0}{\gamma_x} = \lg\frac{\gamma_0^*}{\gamma_x^*} + k_1\sum\sigma_0 + k_2\sum E_s \ , \qquad (26)$$

where E_S is the steric Palm constant. The following equation has been derived[183] for the retention parameters of phenols on silicone OV-225 and neopentyl glycol adipate using the molecular refraction R_0 (I_{St}—data for the standard compound);

$$I = k_1I_{st} + k_2\sum\sigma + k_3\sum R_0 + k_4 \ . \qquad (27)$$

It has been suggested[184,185] that the mean square of the molecular radius be used in combination with the boiling point, or the molecular weight, or the density of the sorbate. The employment of such two-parameter correlations makes it possible to calculate the retention parameters for isoalkanes with s ranging from 1.3 to 5.5 units, the error of the calculation increasing with increase of the number of carbon atoms in the isoalkane molecule.

The single-parameter relations for the retention parameters presented above suffer from a very significant disadvantage: in their derivation it is postulated that the retention in GLC depends only on the properties of the sorbate, i.e. that the stationary phase should not make any contribution to the retention of the sorbate. Such neglect of the influence of the intermolecular interaction in gas-chromatographic solutions cannot fail to be reflected in the accuracy of correlation calculations of this kind. Only single-parameter relations describe the behaviour of the pure sorbate and not the properties of the solution and therefore such relations are at best useful for the description of the retention of small groups of sorbates with similar physicochemical properties using non-specific stationary phases (non-polar phases are best). An increase in the number of parameters in the correlation equation increases the accuracy of the calculation not so much because of the more complete allowance for all the intermolecular interaction factors in solutions as by virtue of the minimisation of the errors in the employment of a large number of empirical proportionality coefficients.

One of the successful trends in the use of two-parameter correlation equations has been developed by Dimov and coworkers[186-194], who postulated a correlation between the Kovats indices and the molar volume and the vapour pressure of the sorbate. In the derivation of correlation equations use is made of the Hildebrand–Scatchard theory of regular solutions, according to which a relation of the following type holds:

$$r = p_{12}^0\overline{V}_{21} \qquad (28)$$

(subscripts 12 and 21 show that the given quantity is the ratio of the corresponding characteristics of substances 1 and 2 being compared). According to this theory, for athermal solutions the free energy of solution is limited by the change in molar entropy on dissolution:

$$\Delta S_s^0 = -R\ln\overline{V}_{21} \ . \qquad (29)$$

The last two relations are based on the so-called physicochemical interaction indices (PCI). However, although two independent parameters of the sorbate were used in the calculations, the accuracy of the calculated data is far from being acceptable: for example, the mean square deviation of the PCI from the experimental values of I for isoparaffins on squalane was 7 units[186]. Such deviations are not surprising bearing in mind that solutions of isoalkanes in a paraffinic stationary phase can never be treated as athermal[195].

The significant errors in the calculation caused Dimov and coworkers to introduce a series of corrections, which are treated as corrections to the entropy of solution (more correctly this was an attempt to compensate for the deficiencies of the extremely simplified model of the gas-chromatographic solution). This correction (SN) was calculated from the following equation:

$$SN = k_1 + k_2X_1 + k_3X_2 + k_4X_3 + k_5X_4 + \ldots \ , \qquad (30)$$

where $X_1 = n_g$, $X_2 = n_{b\text{-}CH_3}/n_L$, $X_3 = (n_b + n_{CH_3})/(n_L + n - n_t)$, $X_4 = n_b n_{CH_3}/n_L(N - n_t)$, n_g is the number of possible conformations of the carbon chain of the molecule, n_b the number of n-butane units in the sorbate molecule, n_L the length of the n-paraffin chain, n_t the number of quaternary carbon atoms, and n the number of carbon atoms in the molecule.

Although Eqn.(30) involves the characteristics of the molecular structure of the sorbate, no justification for this is presented. Thus it reduces to a typical equation for correlations using the regression analysis of the experimental data. As was to be expected, the employment of additional five empirical proportionality coefficients made it possible to reduce the error of the calculation for isoalkanes on squalane to 1.4 units[191]; it must be emphasised that this error characterises interpolation calculations. When attempts were made to extrapolate the relations to higher homologues or isoalkanes with a larger number of carbon atoms in the molecule, the error increased severalfold (for practical GLC, the greatest difficulties arise precisely for alkanes with a large number of carbon atoms in the molecule, for which as a rule there are no published retention characteristics). For example, the employment of the relations obtained[191] in the extrapolation calculations of the parameters I of isoalkanes entails an error of approximately 5 units. The method of Dimov and coworkers has been used for the interpolation calculations of the Kováts indices for alkanes[192], alkylbenzenes[193], and cycloalkanes[194].

It has been suggested that the ratio $I_h/T_b\overline{V}$ (I_h are the retention indices of halogenoalkanes when the standard compounds used in the calculations are not n-alkanes, as for the Kováts indices, but the corresponding halogeno-n-alkanes) be employed for interpolation calculations[196]. For halogenoalkanes, this ratio is approximately constant, but, on passing to more polar sorbents, for example, alcohols on squalane[197], it becomes variable. On the other hand, when stationary phases of the type of Carbowax are used in the separation of n-alkyl alcohols, the above ratio again becomes constant. Thus a necessary condition for the constancy of the ratio is the similarity of the physicochemical properties of the sorbate and the stationary phases. However, even when this condition is observed, the attempt to apply $I/T_b\overline{V}$ as a characteristic of isoalkyl alcohols showed that it depends on the structure of the sorbate molecule[198].

An attempt at a thermodynamic justification of the preferential employment of the entropy factor for the calculation of the retention parameters of hydrocarbons has been made[199] using the Flory–Huggins equations. The free energy of mixing was treated[199] as the sum of the contributions of the entropy of mixing and the residual free energy of solution. Comparison of the calculated and experimental data for isoparaffins on Apiezon M showed that $s = 3$ units for this method. A formula has been proposed[134] for the retention index using the ratios of the molar volumes of the sorbate and the stationary phase. The error of the interpolation calculations using this retention index for C_6–C_8 isoparaffins (stationary phase—squalane) is 1.5 units and is close to the error of experimental data.

Unfortunately, even the two-parameter relations based on the properties of the pure sorbates do not permit the attainment of the required universality in calculations of the retention. It is not fortuituous that the method of calculation using eight additional empirical characteristics, which require the use of computers for the necessary calculations, was described in one of the latest communications by Dimov[200]. An example of the correlation equations proposed by Dimov for isoalkanes is given below[200]:

$$SN = 4.28 - 0.79n_r + 0.27n_i - 0.05n_d + \\ + 2.46n_{CH_3} + 1.50n_b - 2.21n + 0.57n_t \ , \qquad (31)$$

where n_t is the number of branches in the main carbon chain of the sorbate molecule, n_i the number of carbon atoms in the branches of the sorbate molecule, and n_d the number of methylene groups located between the branches of the carbon chain of the sorbate molecule.

Analogous equations have been derived with a series of empirical constants for olefins, cycloalkanes, and alkylbenzenes. In order to set up the necessary computer program, it is necessary to employ the experimental data for 17 to 20 hydrocarbons. The mean square deviation of the calculated data is approximately 2 units. It must be emphasised that all the calculations are of the interpolation type.

Takacs and coworkers[201–207] attempted to use not only the properties of the pure sorbate but also the characteristics of their interaction with the stationary phase for the derivation of correlation equations; this is undoubtedly an advance in the development of scientifically based methods for the calculation of retention in GLC. The properties of the pure sorbate are characterised by the sum of the atomic contribution I_a and the bond contribution I_b, while the interaction with the stationary phase is estimated in terms of the quantity I_i:

$$I = I_a + I_b + I_i + I_m + I_i \ , \qquad (32)$$

where I_m is the molecular index. The computational scheme postulates the additivity of all the increments of the equation, I_a is assumed to be 0.1 of the atomic weight of the given atom, and I_b is calculated by an iterative method from the experimental data using the number of bonds of the same type. The ratio of I_i and I_m was chosen in such a way that it is 25% of I at 100 °C and 25.5% at 50 °C.[201–209] Unfortunately, the correction for the influence of the stationary phase was assumed to be constant for all sorbates, which makes the above concept a variant of correlations with physicochemical properties of sorbates. The advantages of Takacs's method includes the endeavour to treat the retention parameters by resorting to molecular constants, excluding empirical characteristics of the individual sorbates such as the boiling point, the molecular weight, the refraction, etc.

In the calculation of the retention indices of the C_8–C_{10} isoparaffins on squalane the error of the calculation was 1.25 units,[205] which is comparable to the experimental error. In a later study[206] this error was as much as 2.7 units. An attempt has been made[210] to calculate the retention indices of olefins on squalane using the Takacs method; the average standard error (based on interpolation data) was then 16.7 units and for linear undecenes it was 14.5 units. The introduction of new corrections for the calculation of the Kováts indices made it possible to reduce the error to 3.7 units[208]. It has been found[208] that the ratio I_i/I_m is not the same for different sorbates; this to a large extent vitiates the Takacs equation. The large number of empirical parameters and the arbitrary nature of the derivation of the relations in the Takacs approach have been pointed out[211]. However, the approach itself has been applied in a number of subsequent studies. For example, a method has been described[209] for the calculation of I for alkylbenzene on Apiezon L, Carbowax-20M, diethylene adipate, and diethylene sebacate with the aid of a computer. The Kováts indices for alkanes have also been calculated[210].

An increase of the number of factors involved in the calculation is characteristic of many studies in which the retention indices of sorbates are related to physicochemical characteristics. A multifactor correlation equation for the specific retention volume, including the molecular weight of the sorbate M and the π-electron cloud density ρ_π, has been proposed[212,213]; the quantity E_S provides a measure of the steric hindrance to intermolecular interaction:

$$\ln V_g = k_1 M + k_2 \rho_\pi + k_3 E_s + k_4 \ . \qquad (33)$$

The coefficients of this equation are calculated by regression analysis from the experimental retention parameters. However, even this large number of empirical parameters does not enable one to obtain sufficiently accurate results in calculations by Eqn.(33); in the calculation of the V_g for polysubstituted aromatic hydrocarbons the error $s^0 = 25\%$ and can be reduced only by taking into account additional empirical corrections.

Thus the more complex the structure of the sorbate molecule, the greater the number of physicochemical characteristics which must be introduced into the equation for the calculation of retention characteristics. In practice it is impossible to isolate 1–2 dominant physicochemical parameters of the sorbate which would ensure a sufficiently high accuracy of the calculated data. The endeavour of some investigators to employ for this purpose the methods of factorial analysis[214-221], where the maximum number of sorbate parameters are introduced into the computational equations and then the characteristics which influence the retention parameters to the greatest extent are selected on the basis of experimental data, therefore appears to be quite natural.

Studies have shown[214] that the most important parameters of the sorbates are the molecular weight, the molar heat of evaporation, the molar refraction, and the constants of the equation of state. The molecular weight and the molar refraction characterise mainly the energy of dispersion interaction, while the remaining characteristics refer to the overall quantitative estimate of the energy of the interaction of the sorbate molecules with one another. Less important factors are the boiling point and the logarithm of the vapour pressure of the pure sorbate. Its density, dipole moment, vapour pressure, and dielectric constant are parameters for which the correlation with the retention characteristics is very weak. The smallest error of the calculation (approximately 5 units for butyric acid esters) is attained when one of two sets of sorbate parameters is used: (1) the boiling point, the van der Waals constants, the molar refraction, and the specific contribution of the ester group to the intermolecular interaction and (2) the boiling point, the van der Waals constants, the specific contribution of the ester group to the intermolecular interaction, and the number of carbon atoms in the molecule[220]. When an attempt was made to calculate the retention parameters of eighteen aliphatic acid esters on 25 stationary phases, it was shown[222] that the correlation of the results with five sorbate parameters ensures $s = 2.8$ units, an increase of one in the number of parameters employed reducing the error to 2.1 units.

A variant of factorial analysis has been used in studies[223, 224], where the retention factors P of alkylpyridines and ketones were calculated using a parameter proportional to the size of the sorbate molecule x_1, its polarity x_2, the characteristic of the steric environment of the functional groups x_3, and the number of pairs of vicinal alkyl groups x_4:

$$P = k_1 + k_2x_1 + k_3x_2 + k_4x_3 + k_5x_4 \ . \qquad (34)$$

A modification of this equation was presented in a subsequent study by the same workers[225], where the dipole moment of the sorbate molecule (μ) and the number of alkyl substituents in the α-position relative to the functional group (n_0) were used:

$$I = k_1 + k_2n + k_2\mu + k_3n_0 \ . \qquad (35)$$

The last equation was used to calculate the retention parameters of derivatives of aromatic hydrocarbons and pyridine on stationary phases such as Apiezon L, Carbowax 20M, silicone XE-60, and diethylene adipate; $s^0 = 3\%$ for phenols, $s = 56$ for anilines, $s = 14$ for alkylbenzenes, and s is up to 32 units for polar benzene derivatives. Such errors show that the last two equations yield only estimates.

Thus analysis of the attempt to use only the physicochemical characteristics of the sorbate without taking into account intermolecular interaction in gas-chromatographic solutions permits the conclusion that a more or less accurate calculation of retention parameters requires the employment of a number of empirical parameters together with the selected physicochemical constants, which is so large that the complexity of the calculations approaches that of the calculations using topological analysis. Thus the employment of only the characteristics of the sorbate does not lead to the solution of the problem of the calculation of retention parameters, because one then ignores the influence of the stationary phase on the intermolecular interaction in solution. The choice of one or several parameters of sorbates for the calculation of retention parameters can be justified only for a comparatively narrow range of substances and only for interpolation calculations.

The attempts at quantum-mechanical calculations of retention indices using the Hückel method of linear combinations of molecular orbitals are actually close to the above group of methods[226]:

$$I = k_1E + \sum k_2Q_i + k_3, \qquad (36)$$

where E is a dimensionless parameter which depends on the molar volume of the sorbate and the overall energy of the electrons in the molecule and Q_i is the effective charge on the ith atom of the sorbate molecule. The application of Eqn. (36) to the calculation of Kovats indices for cyclohexane derivatives on Apiezon L leads to $s = 14.5$ units. A reduction of the errors to 7–8 units is achieved when E is replaced by the sum of the indices referring to the σ- and π-electrons of the sorbate molecule[227]. The average deviation of the calculated data from the experimental results for 59 derivatives of cholestanyl acetate on SE-30 silicone is 5.7 units, the error increasing to 19.2 units on QF-1 silicone and to 39 units on more polar stationary phases. In calculations for narrow groups of sorbates, the error falls to 0.3 of a unit[226, 228]. The errors of calculations using quantum-mechanical data show that it is undesirable to employ characteristics of this kind: quantum-mechanical calculations for complex molecules are extremely laborious and the information obtained concerning the distribution of electron density in the molecule is only partly employed for calculations on the intermolecular interaction. Finally, the large number of what are essentially empirical parameters in the quantum-mechanical calculations for complex molecules of organic substances makes these methods similar to purely empirical procedures.

GLC practice has shown that the influence of the stationary phase on the retention must be taken into account in all methods for *a priori* calculations. Numerous instances have been described in the literature where a change in the nature of the stationary phase not only alters the relative retention parameters but also alters the sequence in which the substances are eluted from the column. Such phenomena are not reflected in any of the equations quoted in this section of the review. From this standpoint, it would appear to be useful to combine in the computational equations both the properties of the pure sorbates and the characteristics of the stationary phase. The latter quantities can be specified in terms of the Rohrschneider[229] or MacReynolds equations. When the three-parameter Rohrschneider equation is used, the error s in calculations for simple monofunctional sorbates is 12.6 units, while the application of the five-parameter Rohrschneider equation to the same systems lowers the error to 4.1 units. An intermediate error (6 units) has been obtained using the four-parameter Rohrschneider equation[230]. Similar correlations have been used[231] on 14 polysiloxane stationary phases for esters; the correct choice of test substances reduced the

error of the calculation from 6.7 to 4.7 units[232]. The constants of the MacReynolds equation proved to be less suitable for calculations than the corresponding constants of the Rohrschneider equation[233]: the errors for the three-parameter equation reached 30 units.

A series of column parameters and three–four constants of the sorbate have been used in the calculations of the values of I for alcohols, ethers, olefins, and aromatic and aliphatic hydrocarbons on Apiezon L, OV-25 silicone, and 5CP silar[234] with the column temperature programmed in the range from 25° to 250–300 °C. The MacReynolds constants, the molecular weight of the sorbate, its boiling point and molar volume were used. The discrepancies between the calculated and experimental data were 8–10 units.

An attempt to combine factorial analysis with the topo logical method has been described in a study[235], where the advantage of such combinations is emphasised. On the other hand, the influence of the stationary phase on the separation is taken into account by the appropriate choice of test substances, whose initial empirical constants are determined. The nature of these test substances must be as close as possible to that of the substances investigated.

Thus the data examined show that, only by resorting to the characteristics of the interaction of the stationary phase with the sorbate, can one devise an acceptable method for the calculation of the retention parameters of sorbates differing in physicochemical properties. The neglect of the influence of the stationary phase on the retention converts computational methods into specific procedures with extremely limited applications.

IV. THE POSSIBILITY OF USING THEORIES OF SOLUTIONS FOR THE CALCULATION OF RETENTION PARAMETERS

In contrast to the correlations between the retention parameters and the properties of pure sorbates, the application of the theory of non-electrolyte solutions makes it possible to relate the intermolecular interaction energy in solution to the retention parameter of the sorbate. From this standpoint, the employment of theories of solutions is extremely promising for *a priori* calculations of retention parameters. Unfortunately, the lack of a general theory of dilute non-electrolyte solutions or at least of a theory of gas-chromatographic solutions has largely retarded the application of individual variants of theories of solutions to practical calculations of retention parameters. Most of the theories of solutions employed model ideas which simplify unduly the picture of the intermolecular interaction in the gas-chromatographic solution.

Gas-chromatographic solutions have the following specific properties[151]: (a) the concentration of the solution is extremely low and as a rule ranges from 0.1 to 0.001%, (b) the sorbate molecule is much smaller than the molecule of the stationary phase and the intermolecular interaction therefore involves the entire sorbate molecule and part of the molecule of the stationary phase, and (c) the temperature of the stationary phase in the chromatographic column is usually closer to its melting point than to its boiling point, which makes it preferable to use the structure of the solid as an approximation to the structure of the stationary phase. The low concentrations of gas-chromatographic solutions suggest that the main type of interaction in them is that between the sorbate molecules and the surrounding molecules of the stationary phase. The concentration effects in dissolution play only a secondary role for gas-chromatographic solutions, whereas in the classical theories of solutions mainly concentration effects are investigated[1,2].

In comparing data obtained in the classical theory of solutions and the quantities characteristic of GLC, one should note that these two groups of data differ significantly: in the traditional theory of solutions the principal aim is to study the changes in the properties of substances on mixing (the liquid components are mixed), whereas in the study of gas-chromatographic solutions the main question is the alteration of the energy characteristics of the substance when it passes from the gas phase to the solution. The only thermodynamic quantity which has the same significance for the two approaches being compared is the activity coefficient γ and we shall therefore endeavour to confine ourselves to the consideration of attempts at calculations of this parameter.

Many theoretical concepts of the classical theories of non-electrolyte solutions are inapplicable, in principle, to gas-chromatographic solutions. These include all the theories which treat the liquid as a set of solid spherical particles. In view of the wide variety of gas-chromatographic systems consisting of molecules with comparatively complex conformations, only phenomenological theories of solutions can be used for gas-chromatographic calculations.

Since the model of the solid state constitutes the best approximation to the structure of the gas-chromatographic solution, theories treating the liquid as a quasi-crystal lattice have gained great popularity in GLC: each atomic group of the molecules of the stationary phase in the sorbate occupies one site in such a lattice. The ideas of Miller and Guggenheim[236,237] and of Flory and Huggins[238,239] constitute the basis of the equation which represents the excess free energy of solution, proportional to $\ln\gamma$, as the sum of $\ln\gamma^e$ (γ^e reflects the change in intermolecular forces on dissolution) and $\ln\gamma^s$ (this term characterises the entropy contribution due to the different dimensions of the molecules of the stationary phase and the sorbate)[240]. For low values of γ^e, these two parameters can be regarded as independent and then, neglecting the change in the energy of intermolecular forces on dissolution, one can formulate the following equation[241]:

$$\ln\gamma = \ln(1/r_1) + 6\ln\frac{6r_1}{5r_1+1} + \overline{F} \quad , \tag{37}$$

where r_1 is the ratio of the molar volumes of the sorbate and the stationary phase and F the interaction parameter consisting of the enthalpy ($\overline{F}_h$) and entropy components. The following relation is valid for athermal solutions:

$$-\Delta S_s^e/R = \ln(1/r_1) + 6\ln\frac{6r_1}{5r_1+1} + \overline{F}_s \quad , \tag{38}$$

where ΔS_s^e is the excess molar entropy of solution. In some cases $\overline{F}_s$ makes the main contribution to ΔS_s^e.[242] Eqn.(38) has been tested experimentally in relation to the retention parameters of paraffins and cycloparaffins on dinonyl phthalate[243].

A somewhat different form of the Flory–Huggins equation has been proposed for gas-chromatographic calculations[244]:

$$\ln\gamma = \ln r_1 + r_1 + 1 \quad . \tag{39}$$

The authors[244] point out the incorrectness of the representation of r_1 by the ratio of the molar volumes of the sorbate and the stationary phase and suggest that the ratio of the numbers of carbon atoms in the linear chains of the molecules of the sorbate and the stationary phase be used. If it is supposed that $\ln r_1 \ll r_1$, it is possible to derive the following correlation equation[245]:

$$\ln\gamma = k_1 + k_2 r_1 \quad . \tag{40}$$

The Flory–Huggins equation has also been used to calculate the retention parameters of C_1–C_6 alcohols on poly(ethylene glycol)-400;[246] the error s^0 in this method of calculation is 4%.

The Flory–Huggins ideas describe fairly satisfactorily the energy contributions associated with the difference between the sizes of the molecules of the stationary phase and the sorbate; unfortunately the problems of the calculation of $\bar{F}_s$ and $\bar{F}_h$ have been inadequately investigated to date. The Hildebrand–Scatchard theory for regular solutions can be applied to calculations of $\bar{F}_h$ using the so-called solubility parameter $\delta = [(\Delta H_v - RT)/V]^{0.5}$. When the latter is taken into account, Eqn.(36) can be formulated thus:

$$\ln \gamma = \ln(1/r_1) + 6 \ln \frac{6r_1}{5r_1 + 1} + \frac{\bar{V}^*}{RT}(\delta_1^2 - \delta_2^2)^2 , \qquad (41)$$

where $\bar{V}^*$ is the apparent molar volume of the sorbate.

In calculations of the retention parameters of C_5–C_7 isoparaffins, C_6–C_7 olefins, and cycloalkanes with the same number of carbon atoms in the molecule, the error is $s^0 = 1.8\%$.[243] However, the quantity $\bar{V}^*$ is to a large extent formal and all the factors contributing to the entropy of solutions are not reflected in Eqn.(41); furthermore, the need to determine the molar volumes and heats of evaporation increases the difficulty of the preliminary experiments required for calculations involving this equation.

Eqn.(41) is applicable only to systems in which the species are linked solely by dispersion forces. On the other hand, if orientational and inductive forces are manifested in the solution, it is necessary to introduce the corresponding corrections and the last term on the right-hand side of Eqn.(40) assumes the following form[246]:

$$\frac{\bar{V}^*}{RT}[(\delta_1^2 - \delta_2^2)^2 + (\omega_1^2 - \omega_2^2)^2 - f]$$

where

$$(\omega_1^2 - \omega_2^2)^2 = \frac{3.25 \cdot 10^7}{\bar{V}_1^2 RT}(\mu_1^2 \bar{V}_1 + \mu_2^2 \bar{V}_2) .$$

The quantity f is a correction for the negative deviation from Raoult's law. It is actually calculated as the discrepancy between the calculated and experimental data. When this equation is used for interpolation calculations of the retention parameters of hexenes on dimethylformamide, $s^0 = 6.7\%$.[247] The application of the modified Hildebrand–Scatchard equation to polar systems has been discussed in detail[248–250].

When the last equations are employed, there are certain difficulties associated with the necessity to determine the molar volumes of the sorbates and the stationary phase. In order to overcome these difficulties, it is suggested that these characteristics be calculated by indirect methods, for example, from the additive contributions of atomic groups[251] and from the solubility and viscosity[252,253]; it has also been suggested[254,255] that the effective molar volume be used as corrections for the surface tensions of the liquids.

The simplified ideas underlying the Hildebrand–Scatchard theory preclude the attainment of an acceptable accuracy in the calculation of gas-chromatographic retention characteristics for a wide range of compounds. It is difficult to expect that the two-parameter relation for the molar heat of solution as a function of ΔH_v and $\bar{V}$ will describe correctly the entire set of forces acting in a gas-chromatographic solution. The conversion of Eqn.(40) into three- and four-parameter modifications gives rise to only an apparent effect: it is known[214] that, when a three-parameter relation is available, the minimisation of the experimental proportionality coefficients can lead to fairly accurate interpolated data regardless of the nature of the correlation and the parameters employed for it.

It has also been suggested that the parameter $\bar{F}_h$ be evaluated as the mean (geometrical or arithmetical) of the energies of the sorbate and stationary phase molecules[256] or on the basis of Barker's theory[257,258]. The latter ideas have been used in a series of investigations[259–263] in which $\bar{F}_h$ was treated as the result of the interaction between the individual segments of the molecules, which gives the best description of the real pattern of the interaction in the gas-chromatographic solution. The authors[259–263] used the following equation:

$$\bar{F}_h = [q_1(u_1 - u_2)^2 E_i/kT]\, m_2^2 , \qquad (42)$$

where q_1 is the total number of points of contact, u_i the fraction of points of contact of type i for the given molecule, m_2 the mole fraction of the stationary phase in solution, and E_i the interaction energy. It has been postulated that E_i is independent of the medium surrounding the sorbate molecule. It has been shown[264] that the quantity $\bar{F}_h$ characterises the molar enthalpy of mixing. Barker's theory has also been used to calculate the retention parameters of alkanes[265–268], but no quantitative estimates of the accuracy of the method employed are indicated.

Prigogine's theory of solutions has been modified for gas-chromatographic systems[269]:

$$\bar{F}_h = h_1 k_i / 4RT, \quad \bar{F}_s = k_1(\lambda + k_i)^2/2R,$$
$$\lambda = 1 - (k_n/\bar{r})_2 (k_n/\bar{r})_1, \quad k_i = (\varepsilon_{22} - \varepsilon_{11})/\varepsilon_{22} , \qquad (43)$$

where $3k_n/\bar{r}$ is the number of external degrees of freedom of the molecular segment, k_i a constant proportional to the depth of the potential well for the 1–1 and 2–2 interactions of the substances and determined from the critical temperature and the volume of the hard spheres, h_1 the configurational enthalpy, k_n the configurational heat capacity, and ε the interspecies interaction potential. The quantity $k_n/\bar{r}$ can be determined directly. An empirical equation involving the number of segments in the sorbate molecule has been proposed for this purpose[269].

The activity coefficients of C_4–C_{10} n-alkanes in C_{22}–C_{36} n-paraffin stationary phases have been calculated to test Eqns.(43).[244] The experimental data showed that the ratio $k_n/\bar{r}$ increases linearly with the number of carbon atoms in the molecule of the stationary phase (the stationary phase is designated by subscript 2 and the sorbate by subscript 1). The authors[244] used the following equation for their calculations:

$$\bar{F} = 18(n_1 + 1)[1/(n_2 + 1) - 1/(n_1 + 1)]^2 \cdot E_i/kT . \qquad (44)$$

The configurational enthalpy and the parameter k_i were calculated from the formulae

$$h_1 = \Delta H_v + RT \qquad (45)$$

$$k_i = \frac{T_2^c \tilde{V}_2^{1/3}}{T_1^c \tilde{V}_1^{1/3}} - 1 \qquad (46)$$

where subscript c refers to the critical parameter and $\tilde{V}$ is the van der Waals volume.

The relative average standard deviation of the calculated quantities from the experimental data was 0.8%. According to the authors[244], the question of the influence of $\bar{F}_s$ on the retention parameters remained unelucidated in view of the inadequate accuracy of the experimental results. On the other hand, it has been claimed[270] that $\bar{F}$ is wholly determined by $\bar{F}_s$, while $\bar{F}_h$ has the greatest influence on the experimental error. In fact, however, the neglect or underestimate of the contribution of any of the components of $\bar{F}$ to the retention parameter distorts the real pattern of the intermolecular interaction in gas-chromatographic solutions, where the influences of the entropy and enthalpy of solution on the free energy of solution are comparable.

Prigogine's theory of solutions has been used[271] to describe the properties of solutions of benzene in polyphenyl stationary phases. The entropy of mixing was calculated on the basis of the lattice model of the liquid state and the energy

of the intermolecular forces was calculated using the theorem of corresponding states, although the latter employs a number of assumptions which are by no means correct.

The group method[271] operates, in conformity with its physical significance, also with two components of the free energy of the interaction of the sorbate with the stationary phase, namely the entropy component γ_S, calculated from the Flory–Huggins equation, and the group component γ_j, calculated from the equation

$$\gamma_j = n_{mj}(\lg\gamma_m - \lg\gamma_m^*) \quad , \qquad (47)$$

where n_{mj} is the number of groups k in the molecule j, γ_m the activity coefficient of the structural group k in solution, and γ_m^* the activity coefficient of group k in the pure solvent. After a series of simplifications, the following equation has been proposed for homologous series of sorbates, incorporating the constants of the interactions of individual structural groups[272]:

$$\lg\gamma = k_1 + k_2/(n_1 + k_3) + k_4k_5/n_1 + \\ + n_2/(k_5 + n_2) + k_6(k_5 - n_1)^2 \quad . \qquad (48)$$

All the constants in Eqn.(48) (from k_1 to k_6) are determined experimentally with the aid of test sorbates. The error of the calculated data is in this case 5–10%.

The relations for the calculation of the energy of intermolecular interaction by the method of the group theory have been examined in a general form[273,274]. It has been postulated that the interaction energy is additive with respect to the structural groups of the molecule in the stationary phase and the sorbate (the groups m_i^v and m_i^u respectively). For dilute binary solutions, the excess molar heat of solution is calculated from the equation

$$\Delta H_s^e = k_{12}s_1 \quad , \qquad (49)$$

where

$$k_{ij} = -\sum_{uv} k^{uv}(m_i^u/s_i - m_j^u/s_j)(m_i^v/s_i - m_j^v/s_j)s^u s^v,$$

$$s_i = \sum m_i^u s^u, \quad k^{uv} = \varepsilon^{uv} - 0.5(\varepsilon^{uu} + \varepsilon^{vv}) \quad .$$

Comparison of the calculated and experimental molar heats of solution of hydrocarbons of different classes shows that the average standard error of the calculation is 0.14 kJ mol^{-1}. It has been noted that the molar entropies of mixing of hydrocarbons calculated from the Flory–Huggins equation differ from the experimental values by a factor of 10–20. This shows that the description of the entropy of solution cannot be restricted to a single factor—the different dimensions of the molecules of the sorbate and the stationary phase. As shown in the next section, the entropy of solution consists of 4–5 main components, among which the factor associated with the differences between the dimensions of the molecules of the sorbate and the stationary phase is not the main one.

Calculations of the activity coefficients by the group method showed[274] that s^0 = 1.6% for acids in water, 4.5% for alcohols in water, 2.4% for alcohols in paraffins, 5% for ketones in paraffins, 5–8% for cycloalkanes in heptane, and 5–13% for paraffins and cycloalkanes in triethylene glycol. It is noteworthy that the errors of the calculation are smaller for extremely non-ideal systems such as those in alcohols and paraffins, while for solutions close to ideality (solutions of hydrocarbons in hydrocarbons) the errors of the calculation are large. This apparently indicates an unsuccessful choice of test substances for the determination of the empirical coefficients in the case of non-polar and weakly polar systems, while the final result of the calculation depends on the intuition of the investigator, as in factorial analysis. In the model of the group theory, the activity coefficients are calculated using a large number of empirical corrections introduced in the form of interaction coefficients and the effective cross-sections (encounter probabilities) of individual structural groups $s^{u,v}$. Despite this, the given model is closest to the approach based on the theory of group additivity and examined in Section II of this review. The errors themselves are also of the same order of magnitude as for the purely empirical methods for the calculation of retention parameters.

The application of the free volume theory to the calculation of the activity coefficients of spherical molecules has been described[275]. According to this theory, the potential energy of the liquid depends on the difference between its real volume and its calculated van der Waals volume. The introduction of a series of simplifying assumptions made it possible to calculate the activity coefficients of a number of molecules containing germanium, silicon, and titanium; the errors of the calculation proved to be smaller than those arising in the application of the Guggenheim and Hildebrand–Scatchard theories. A number of inorganic compounds have been investigated in a study[276,277] where the free volume theory was also used for the calculations.

The theory of conformal solutions[278], the theory of athermal solutions[278,279], and the theory of regular solutions[241] have also been used to calculate the retention parameters. The last two theories are more suitable for correlation calculations, because the concepts of athermal and regular solutions are invalid for real gas-chromatographic solutions.

The study of the statistical thermodynamics of solutions constitutes one of the trends in the theory of solutions, which are promising from the standpoint of their application to GLC: no model ideas, i.e. ideas simplifying the real picture of the interaction, are then put forward. The energy of the intermolecular interaction is calculated as the sum of the elementary functions of state of the molecules in solution: the intermolecular interaction energy of each conformation of the molecule and its statistical weight. However, the *a priori* determination of these parameters still encounters difficulties which cannot be overcome and which are associated with the inadequacy of our information about the real conformations and interactions of the molecules in solution. Nevertheless certain ideas on statistical thermodynamics have begun to be used in calculations of the relative retention; for example, the relative retentions of the stereoisomers of substituted cyclohexanoic acids have been calculated[280], with errors ranging from 0.1 to 1.5%, from the ratio of the partition functions based on the parameters of the rotational spectra of the molecules.

Analysis of the data described in this section permits certain conclusions concerning the possibility of employing the theories of solutions for the calculation of retention parameters in GLC. According to some results[151,269], three main factors contribute to the excess free energy of solution in GLC: (a) the geometrical effects arising as a consequence of the difference between the sizes of the molecules of the stationary phase and the sorbate (see the Flory–Huggins theory); (b) the energy effect associated with the energy of the intermolecular forces in solution ($\bar{F}_n$); (c) the structural effect associated with the change in the conformation of the molecule on dissolution and with the restriction of the number of degrees of freedom on passing from the gas to the liquid phase ($\bar{F}_s$). The effect (a) has been fairly thoroughly investigated and has been described mathematically, but its contribution does not always exceed 5–10% even to the entropy of solution. For the remaining two effects, the modern theories of dilute non-electrolyte solutions cannot provide an adequately accurate mathematical description, which is the reason why workers in the field of chromatography have been disappointed by the application of theories of solutions to the calculation of retention parameters in GLC. The significant model limitations (hard spheres, theorem of corresponding states, etc.) of solution theories preclude

their application to the description of the properties of a wide variety of gas-chromatographic systems. The introduction of additional empirical parameters lowers the value of solution theories to the level of the methods of empirical calculations of retention parameters.

V. SEMIEMPIRICAL CALCULATIONS OF THE MOLAR HEATS AND ENTROPIES OF SOLUTION

Most of the studies on the application of solution theories in calculations of retention parameters are associated with the evaluation of the activity coefficients, which are not in general direct retention characteristics: the calculation of activity coefficients requires (in the ideal case) the availability of data on the fugacity or (usually) the movement of the saturated sorbate vapour. At the same time the determination of thermodynamic functions for the phase equilibrium in gas-chromatographic systems does not require any information at all about the vapour pressure or fugacities of sorbates, i.e. such information in no way assists in the calculation of retention parameters. Furthermore, the molar free energy of solution (the free energy of the phase transition) as well as quantities proportional to it (I and $\ln V_N$) are hardly susceptible to calculation by additivity methods or methods involving the employment of correlations between the retention parameters and the physicochemical properties of the sorbates.

Consequently it is useful to seek a compromise, which combines the main advantages of the theoretical foundations of the intermolecular interaction, the solution theories, the correlations with physicochemical properties, and the additive contribution of individual atomic groups to the interaction energy. We believe that the application of these ideas is possible in the separate analysis of two main components of the molar free energy of solution—the molar heat of solution and the molar entropy of solution. A series of ideas in statistical thermodynamics and molecular physics can be related to each of these thermodynamic quantities, including the experience accumulated in the employment of the physicochemical characteristics of sorbates and stationary phases as well as purely empirical approximations.

In a series of studies of Sakharov and coworkers[281-288] gas-chromatographic solutions have been treated as quasi-crystalline lattices and the molar heats of solution ΔH_s have been treated as the sum of the energy of intermolecular forces and the work of formation of a hole within the solvent in which the sorbate molecule is accommodated. If the treatment is restricted to isomeric substances, then the molar heat of formation of the hole ΔH_h can be neglected for comparative calculations. The energy of intermolecular forces $\Delta H_s - RT$ can be quite correctly represented as the sum of the increments (ΔH_i) due to individual atoms (or groups of atoms) in the sorbate molecule. The energy of the intermolecular forces between the nth atom of the sorbate molecule and the stationary phase is calculated as the difference between the energy of the interaction of an isolated nth atom with the stationary phase E_n and the quantity E'_n reflecting the intermolecular shielding of the same atom in the sorbate molecule, i.e. ΔH_n represents the effective interaction of the nth atom with the stationary phase. It has been postulated[281-288] that the values of $\Sigma E'_n$ for isomeric compounds are identical and that $\Delta\Sigma E_n$ represents the difference between the molar heats of formation of these isomers (this claim is not altogether correct). Finally, it has been suggested that the molar entropy of solution is proportional to the molar heat of solution or, in other words, that the molar free energy depends solely on the molar heat of solution.

Linear correlations between $\ln r$ and the difference between the molar heats of formation of isomers have been found experimentally for C_4–C_7 alkanes and cycloalkanes using a non-polar stationary phase. This made it possible to formulate the following rule: "of two isomers with similar structure, the resonance and polar factors in the molecules of which are equal, the isomer with the greater (molar) heat of solution in the non-polar solvent has a smaller (molar) heat of formation"[281]. It is noteworthy that the suggested analogy between the energy of intermolecular forces in solution and the energy of formation of the molecule is formal, which is the reason for the considerable scatter of experimental points in many instances relative to the calculated relations. For example, the relations between the Kováts indices of isomeric olefins and their molar heats of formation[285] consist of a family of straight lines with different slopes and each straight line corresponds to a group of isomers with the same number of branches in the carbon chain around the double bond. Similar relations have been found for alkylbenzenes and certain other classes of compounds. The disadvantages of this concept include the correlation of the retention characteristics solely with the properties of the isomers being separated and the neglect of the influence of the stationary phase on the retention.

It is noteworthy that the approach of Sakharov and coworkers to the treatment of the intermolecular interaction in gas-chromatographic solutions has yet another positive aspect: attention is concentrated on the evaluation of the relative retention parameters r and I. Indeed, in GLC practice the main criterion of the selectivity of the stationary phase is the relative retention parameter which makes it possible to infer whether the separation of the relevant sorbates ($r \neq 1$) on a given stationary phase is possible and how difficult it is to achieve (the value of r and to some extent the value of V_N or V_g). The simplicity of the calculation of the relative retention parameters from experimental data, the low experimental error in the determination of these quantities, and their simplified theoretical treatment, where the effects of many factors cancel out made the relative retention parameters the most popular in GLC practice at the same time and, which is no less important, the most reproducible[289]. The principal thermodynamic relations between the relative retention parameters and the intermolecular interaction parameters are fairly simple (the superscript 0 denotes a relative molar thermodynamic function):

$$\Delta G_s^0 = -RT \ln r = \Delta H_s^0 - T\Delta S_s^0 \quad . \qquad (50)$$

It is therefore useful to describe briefly the semiempirical concept underlying the calculation of the relative molar thermodynamic functions of dissolution[290-292]. In this concept the gas-chromatographic solution is regarded as a quasi-crystalline lattice where each site is occupied by an atom (or atomic group incorporating all the chemically linked hydrogen atoms). Since the sorbate molecule is surrounded on all sides by the molecules of the stationary phase (infinitely dilute solution), the calculation of the intermolecular interaction in the given system reduces to the calculation of the energy of the interaction between the atomic groups of the sorbate molecules and the surrounding atomic groups of the stationary phase, and the relative positions of the molecules must be selected on the basis of the minimum potential energy of the system.

In conformity with the traditional ideas concerning the formation of a solution, the experimental molar heat of solution ΔH_S can be represented as the sum of the energy of the intermolecular forces between the sorbate molecule and the stationary phase E_i, the molar heat of formation of the hole, and the term RT reflecting the change in the energy of the

system on condensation of the ideal gas into the liquid phase:

$$\Delta H_s = E_i + \Delta H_h + RT \quad . \tag{51}$$

If the treatment is restricted to systems with dispersion interaction, the calculation of the energy of intermolecular forces is feasible. Sakharov[281] proposed the following equation for the energy of the dispersion interaction of the *i*th atom with the stationary phase:

$$U_d = -0.9 \int_{r_i+r_0}^{\infty} 0.75h\nu \frac{\alpha_i \cdot 4\pi r^2 \bar{\rho}}{r^6} dr = 0.9\pi h\nu \frac{\alpha_i \bar{\rho}}{(r_i + r_1)^3} \quad , \tag{52}$$

where α is the polarisability, $\bar{\rho}$ the density of the polarisability of the medium, i.e. of the stationary phase (the ratio of the molar refraction to the molar volume of the stationary phase), r_i the van der Waals radius of the *i*th atom, h the Planck constant, ν the average vibration frequency of the molecules of the stationary phase with the *i*th atom, and r_1 the average van der Waals radius of the functional groups of the stationary phase. Sakharov suggested that the quantity $D = \alpha_i/(r_i + r_1)^3$ be called the "dispersity" of the atom or atomic group and demonstrated, by analysing the literature data, a correlation between the Kováts index and the "dispersity".

A somewhat simpler relation between the dispersion interaction and the molar heats of solution in a non-polar stationary phase has been derived differently[290]. The dispersion interaction energy of a pair of fairly remote spherical particles (the distance between them is greater than the covalent radius) is described by an equation which includes the polarisabilities of the atomic groups of the sorbate (α_i) and the stationary phase (α_2):

$$U_d = -k\alpha_i\alpha_2\bar{r}^6 \quad . \tag{53}$$

When the interaction of atoms or atomic groups in a gas-chromatographic solution is considered, then Eqn.(53) is valid. On replacing the atomic polarisability by the atomic refraction R_0, we obtain the equation

$$D_n = R_{0i}R_{02}/(\bar{r}_i + \bar{r}_2)^6 \quad . \tag{54}$$

Indeed the linear correlation between ΔH_S and ΣD_n holds for a number of classes of non-polar and moderately polar compounds[293,294].

If the term $\bar{r}_1 + \bar{r}_2$ is represented as the sum of the van der Waals radii of an atom (or atomic group) in the sorbate and an atom (atomic group) in the stationary phase, then the values of D_S can be readily tabulated for all the atoms and atomic groups incorporating chemically bound hydrogen atoms[291]. The constants of the intramolecular shielding of the atoms or atomic groups of the sorbate can be readily calculated on the basis of the species constructed taking into account stereochemical ideas[295]. Thus the increments of the energy of the dispersion interaction of the atoms and atomic groups of the sorbate molecule with the medium (stationary phase) can be calculated from the molecular characteristics[290,291]. The quantity E_i is calculated as the sum of n increments due to the atomic groups of the molecule:

$$E_i = i \sum_n K_n D_n \quad , \tag{55}$$

where i is the normalising multiplier and K_n the coefficient of the intramolecular shielding of the atomic group of the sorbate. The normalising coefficient is calculated from the experimental molar heats of solution of n-paraffins and takes into account the influence of the real non-polar medium on the molar heat of solution. It varies non-linearly with the number of carbon atoms in the n-paraffin molecule, approaching exponentially a limiting value at $n > 7$.

Allowance for the work of formation of a hole in the gas-chromatographic solution is a difficult problem, whose solution depends on the real structure of the stationary phase. It has been suggested[283,296] that the work of formation of a hole in the solvent is proportional to the surface tension of the stationary phase and the surface area of the sorbate molecule. However, such hypotheses are valid only for a structureless stationary phase, which can be represented approximately as a system of randomly distributed small spherical molecules. The real stationary phases in GLC consist of an anisotropic medium with a distinct structure, which has been confirmed by X-ray diffraction studies[297]. For example, liquid paraffin stationary phases constitute a system of mutually oriented linear hydrocarbon chains, which migrate freely in parallel planes with a minimal energy expenditure. Therefore, if the accommodation of the sorbate molecule in a paraffin stationary phase requires merely a shift of a paraffin molecule in a parallel plane (longitudinal shift), then the work of formation of a hole is minimal; this applies to the dissolution of n-paraffins; the work of formation of a hole in n-paraffins is assumed to be zero in comparative calculations. On the other hand, when the structure of the stationary phase changes on dissolution, then the work of formation of the hole can no longer be neglected. For example, on dissolution of a branched isoparaffin in an n-paraffin stationary phase the molecules of the stationary phase move apart in a plane at right angles to their longitudinal axis (transverse shift). In the transverse shift of the molecules of the stationary phase the work of formation of a hole is proportional to the number of branches of the hydrocarbon chain of the sorbate molecule, although in the general case the relative positions of the branches also influence the work of formation of the hole[291,298].

In the chromatography of polar sorbates on non-polar or weakly polar stationary phases, a new factor appears—the concentration effect Δk,[299–304] which is due to the association of the molecules of the polar sorbate in the non-polar solvent, which occurs even at infinitesimal concentrations of the solution. The effect is particularly large for alcohols and other sorbates forming a hydrogen bond (approximately 14 kJ mol^{-1}); for the remaining polar sorbates, the energy of the concentration effect is approximately 3–6 kJ mol^{-1}.[301]

In the determination of the energy of intermolecular forces of polar sorbates in polar stationary phases account must be taken of the orientation interaction, which arises under the influence of the dipole moments of the functional groups of the stationary phase and the sorbates, which are determined by stereochemical factors. The bond microdipoles are partly shielded by the chemically linked atoms or atomic groups; apart from the bond microdipoles, the so-called secondary dipoles, formed by chemically non-linked atoms or atomic groups, participate in the orientation interaction. The contribution of the orientation interaction to the energy of the intermolecular forces can be determined solely by considering specific systems with allowance for the optimum relative positions of the molecules of the sorbate in the stationary phase. Examples of the determination of the extent of the orientation interaction in gas-chromatographic systems have been published[305–307].

The intermolecular forces in solutions of aromatic and other cyclic molecules must be calculated taking into account the relative spatial distribution of the molecules, the electronic effects of various substituents in the aromatic ring, and a number of other features characteristic of systems with steric hindrance to interaction. These questions have been discussed in detail[304,308–316].

The calculation of the relative molar entropy of solution for gas-chromatographic systems involves considerable difficulties. It follows from Section IV that the application of the

Flory–Huggins equation alone to the solution of this problem is inadequate. The difference between the molar entropies of the sorbate in the gas phase and in solution ΔS_S is determined by the following factors[317]. In the gas phase the entropy of the molecule includes the entropy of the rotational movement S_r [the sum of the entropies of the internal (S_{ri}) and external (S_{re}) rotational movements], the electronic entropy, the vibrational entropy, the nuclear components, and the translational entropy S_{tr}. On passing to the solution, the sorbate molecule loses some of its degree of freedom, i.e. the entropy decreases and the molar entropy of solution, calculated from gas-chromatographic data, is therefore always negative. The decrease of the entropy of sorbate molecules is determined primarily by the decrease in the rotational and translational entropies; as a consequence of the comparatively weak intermolecular forces in gas-chromatographic solutions, the remaining forms of the entropy of the sorbate molecules do not change on passing from the gas to the liquid phase.

Using the fundamental relations of statistical thermodynamics[318], it is possible to formulate the equation

$$\Delta S_{tr} = R \ln V^0 - k_1 , \qquad (56)$$

where V^0 is the molar volume of the ideal liquid related to the van der Waals molar volume of this liquid by the equation

$$RT \ln V^0 = R \ln M - R \ln \tilde{V} + k_2 . \qquad (57)$$

Eqn.(56) characterises the change in the translational entropy when the sorbate molecules pass from the gas to the liquid phase.

The so-called compensation effect[319], observed for many gas-chromatographic systems[320–323], makes a definite contribution to the entropy of solution. The essential feature of this effect consists in the linear relation between ΔS_S and ΔH_S for many simple systems, whose slope is an inverse function of temperature. The following equation is then obtained for the relative molar entropy of solution (the ratio for the sorbates x and r):

$$\Delta S_S^0 = \Delta H_S^0 T / k_1 + R \ln (M_x / M_r) - R \ln (\tilde{V}_x / \tilde{V}_r) + \Delta S_{re}^0 + \Delta S_{ri}^0 . \qquad (58)$$

For isomeric compounds, the values of $\tilde{V}$ are approximately the same. Calculations of the molar entropy of solution have been performed in a number of studies[308,324,325], where the influence of a change in the rotational entropy on ΔS_r was demonstrated.

The thermodynamic approach to the calculation of the molar heat and entropy of solution described above makes it possible not only to calculate the individual thermodynamic functions of solution but also to calculate, using their combination, the overall parameters of the selectivity of the stationary phase—the Kováts index and the relative retention, and the knowledge of the relative molar heats of solution makes it possible to calculate these quantities for any column temperature.

The given method makes it possible to obtain fairly accurately extrapolated retention parameters for extremely complex molecules. For example, the Kováts indices for C_9 and C_{10} isoparaffins on squalane have been calculated with an average standard error of 2.2 units[298]. Such an accuracy of extrapolation calculations is not ensured by any of the other methods considered in this review. The standard error of the calculation of the Kováts indices of C_7 and C_8 olefins on squalane by the same method proved to be 5.2 units, which is also the best result for such systems. In calculations of this kind, one introduces initially specific relations associated with the characteristics of the interaction of the individual structural groups of the sorbate molecules with the stationary phase and then these are used in the evaluation of the thermodynamic functions of solution, from which the Kováts indices are calculated.

Analysis of different investigations has shown that each group of methods has definite advantages and that at the present stage of the development of the theory of non-electrolyte solutions one cannot neglect any of these procedures.

When fairly extensive experimental data for test sorbates, grouped in specific series, are available, the optimum interpolated retention parameters can be calculated empirically by combining the methods of the topological and factorial analyses with the constants (for example, constants of the Rohrschneider type) for the stationary phase.

For interpolation calculations within narrow groups of sorbates with similar physicochemical properties, it is most rational to employ the correlations between the retention parameters and the physicochemical properties of the sorbates. The calculation of the thermodynamic functions of solution is possible only after a detailed analysis of the characteristics of the intermolecular interactions in the systems investigated. However, these are not only interpolation but also extrapolation calculations, which is particularly important for high-molecular-weight sorbates, whose retention parameters are usually unknown. The accuracy of the calculations using the fundamental functions of solution is highest among the methods considered.

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Reactions of Peroxydisulphuryl Difluoride and Halogen Fluorosulphates with Organic Compounds

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The literature data on the reactions of peroxydisulphuryl difluoride and halogenofluorosulphates with various classes of organic compounds and on the methods of synthesis and properties of the above reagents are surveyed and described systematically. Attention is concentrated on the possibility of selective reactions which apparently predetermine the subsequent extensive employment of peroxydisulphuryl difluoride and halogen fluorosulphates for synthetic purposes. The bibliography includes 226 references.

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I. INTRODUCTION

Peroxydisulphuryl difluoride $(OSO_2F)_2$ and halogen fluorosulphates $HalOSO_2F$, which were first synthesised at the end of the 1950's and the beginning of the 1960's[1-7], have comparatively recently attracted the attention of organic chemists as exceptionally active reagents permitting in a number of instances reactions which had not been feasible hitherto and a deeper understanding of the nature of the reactivities of many organic compounds, including those which had been previously regarded as the most inert.

Peroxydisulphuryl difluoride and halogen fluorosulphates are genetically related although their reactivities are to some extent different.

Peroxydisulphuryl difluoride—the peroxide of fluorosulphonic acid—differs from the majority of the known peroxides by the complete absence of explosive properties and a high stability in a pure state. By virtue of its structure, it is capable of supplying the $\dot{O}SO_2F$ radical, and is usually regarded as one of the most effective radical reagents. However, direct oxidations, which have been most thoroughly investigated in the case of inorganic substances, are also known.

Halogen fluorosulphates are mixed anhydrides of the corresponding halogen oxy-acids (for example hypochlorous and hypobromous) and fluorosulphonic acid. The name "halogenofluorosulphates" is used together with "halogen fluorosulphate".

In view of the similarity of the electronegativities of the fluorine atom and the fluorosulphate group, reactions of the radical type are more characteristic of fluorine fluorosulphate. In chlorine, bromine, and iodine fluorosulphates the halogen atoms carry a positive charge as a result of polarisation, so that these compounds are extremely effective electrophiles.

Since peroxydisulphuryl difluoride has been hitherto an essential precursor of halogen fluorosulphates (except fluorine fluorosulphate), its properties have naturally been investigated to a greater extent.

To ensure a compact exposition of the relevant data, in addition to the nomenclature generally adopted (such as, for example, the term methyl fluorosulphate CH_3OSO_2F), in a number of instances, as in the majority of original communications, the fluorosulphate group has been treated as a substituent: for example, bis(fluorosulphato)dichloromethane $CCl_2(OSO_2F)_2$ and tetrakis(fluorosulphato)methane $C(OSO_2F)_4$.

Individual questions of the chemistry of peroxydisulphuryl difluoride and halogen fluorosulphates have been dealt with in a number of publications[8-10], but sufficiently complete surveys are not available and in the present review an attempt has been made to make good this deficiency.

II. PROPERTIES OF PEROXYDISULPHURYL DIFLUORIDE AND HALOGEN FLUOROSULPHATES

Peroxydisulphuryl difluoride and chlorine and bromine fluorosulphates are low-boiling liquids, fluorine fluorosulphate is a gas, and iodine fluorosulphate and bromine and iodine trisfluorosulphates are readily fusible substances (see Table). The infrared and Raman spectra[3,11,22-29] as well as ^{19}F NMR spectra[3,7,12,30-36] of the above compounds have been studied in detail.

The high reactivity of peroxydisulphuryl difluoride is due to the ease of its dissociation into radicals[3,14-19,37]:

$$S_2O_6F_2 \rightleftarrows 2OSO_2F \quad .$$

The molar dissociation energies of the O—O bond in peroxydisulphuryl difluoride and of the O—Hal bond in chlorine and fluorine fluorosulphates are listed in the Table. A calculation has been performed for the fluorosulphate radical by the LCAO-MO SCF method[38] and studies have been made of its infrared spectrum[39], its absorption spectrum in the visible region[14,15,40-42], and its fluorescence spectrum excited by laser radiation[43-46].

Solutions of peroxydisulphuryl difluoride in fluorosulphonic acid are not conducting[47], in contrast to solutions of, for example, iodine fluorosulphate[13].

Peroxydisulphuryl difluoride and halogen fluorosulphates are highly reactive compounds. They are best stored (except fluorine fluorosulphate) in sealed glass tubes, when no changes are observed in the specimen even after several months. The majority of the reactions can be carried out in

apparatus made of Pyrex glass, but at elevated temperatures quartz, Teflon, stainless steel, nickel, and monel metal are usually employed.

Certain physicochemical properties of peroxydisulphuryl difluoride and halogen fluorosulphates*.

Compound	M.p., °C	B.p., °C**	d_4, g cm^{-3} (t, °C)	References	E, kJ mol^{-1}	λ_{vap}, kJ mol^{-1}	Trouton's constant	References
$(FSO_2O)_2$	−55.4	67.1	1.6450 (35.5)	[3]	92.048***	31.882	22.4	[3]
$FOSO_2F$	−158.5	−31.3	—	[2]	138.072±1.225	—	—	[20]
$ClOSO_2F$ ****	−84.3	45.1	1.711 (20)	[7]	188.280±6.276	32.049	24.0	[7, 21]
$BrOSO_2F$ *****	−31.5	117.3	2.238 (25)	[12]	—	36.275	22.05	[6]
$Br(OSO_2F)_3$	59	—	—	[6]	—	—	—	—
$IOSO_2F$	51.5	200	—	[13]	—	—	—	—
$I(OSO_2F)_3$	32.2	—	—	[6]	—	—	—	—

*Note: E is the dissociation energy of the O–O or O–Hal bonds and λ_{vap} is the latent heat of evaporation.

**At 760 mmHg.

***Other values of E: 91.221 ± 0.628 kJ mol^{-1};[14] 94.487 kJ mol^{-1};[15] 112.968 kJ mol^{-1};[16] 104.60 kJ mol^{-1};[17] 93.722 ± 3.766 kJ mol^{-1}.[18,19]

****According to the results of Schack and Wilson[11], the boiling point is 43.4 °C, λ_{vap} = 31.610 kJ mol^{-1}, and Trouton's constant is 23.8.

*****According to the results of Roberts and Cady[6], the boiling point is 120.5 °C and d_4^{25} = 2.600 g cm^{-3}.

In contrast to organic compounds, peroxydisulphuryl difluoride and chlorine, bromine, and iodine fluorosulphates are insensitive to external influences (impact, brief contact with an open flame) and to changes in phase state, but fluorine fluorosulphate has shown a high tendency towards explosive decomposition even at temperatures below 0°C[48], which is apparently characteristic of liquefied $FOSO_2F$. The usual thermal decomposition of fluorine fluorosulphate at 236–263 °C leads to sulphuryl fluoride and oxygen[49], while in the presence of chlorine at 90–110 °C the products are peroxydisulphuryl difluoride, chlorine monofluoride, and a small amount of chlorine fluorosulphate[50]. Both reactions have been studied kinetically and the calculated data agree satisfactorily with experiment[51].

Both peroxydisulphuryl difluoride and halogen fluorosulphates react vigorously at room temperature with traces of moisture, benzene, acetone, and other organic compounds (sometimes with inflammation). Liquid chlorine fluorosulphate and peroxydisulphuryl difluoride ignite incompletely fluorinated greases. At low temperatures peroxydisulphuryl difluoride is much less reactive than chlorine and particularly bromine fluorosulphate. Peroxydisulphuryl difluoride therefore tends to accumulate in the reaction mass in many instances; as the temperature is raised, this can be the cause of a vigorous reaction and ejection of the mixture. Peroxydisulphuryl difluoride behaves analogously also in water containing ice, where it is initially precipitated as the lower layer.

The facts presented indicate the highly corrosive nature of the reagents; experiments employing them require reliable protection from atmospheric moisture, are potentially dangerous, must be carried out with adequate caution, and protective measures must be taken.

In order to increase the selectivity of the reactions, usually reduced temperatures (down to −100 °C), inert (highly fluorinated) solvents, very slow mixing of the reactants (for example, by diffusion *in vacuo*), and similar procedures are used. The method of generating peroxydisulphuryl difluoride *in situ* by an electrochemical method is apparently extremely promising[52–54].

In a more detailed consideration of the properties of peroxydisulphuryl difluoride and halogen fluorosulphates one must emphasise that they react vigorously with many elements (the reactions of peroxydisulphuryl difluoride with the halogens described in the next section) and their hydrides, oxides, peroxides, and salts.

Peroxydisulphuryl difluoride readily oxidises sulphur[55–57], selenium[58,59], tellurium[60,61], and antimony[62], complex cations being formed in the first stage, for example[56,57]:

$$2S_8 + (OSO_2F)_2 \xrightarrow[HSO_3F]{t^\circ} S_{16}^{+2}(OSO_2F^-)_2 \quad \text{(red soln)}$$

$$S_8 + (OSO_2F)_2 \xrightarrow[HSO_3F]{0^\circ} S_8^{+2}(OSO_2F^-)_2 \quad \text{(blue soln)}$$

Many salts of fluorosulphonic acid, including complex salts, have been obtained by treating metals and their oxides or salts with peroxydisulphuryl difluoride (data up to 1972 inclusive have been surveyed in a review[9]) or halogen fluorosulphates; vigorous research is being continued[63–73], for example, the following methods of synthesis have been proposed[67,73]:

$$Ag + (OSO_2F)_2 \rightarrow Ag(OSO_2F)_2$$

$$Au + BrOSO_2F \rightarrow Br_3[Au(SO_3F)_4]$$

Fluorine fluorosulphate readily fluorinates not only salts[74], bromine[7], and iodine[75], but also xenon at 170–180 °C[76]:

$$FOSO_2F \xrightarrow{CsOSF_5} SF_5OF$$

$$FOSO_2F \xrightarrow{I_2} IF_3(OSO_2F)_2 + (OSO_2F)_2$$

$$FOSO_2F \xrightarrow{Xe} XeF_2 + (OSO_2F)_2$$

Peroxydisulphuryl difluoride reacts vigorously with ammonia, hydrogen sulphide, and hydrogen chloride[77]; chlorine fluorosulphate also readily reacts with the last substance[78]:

$$HCl + ClOSO_2F \rightarrow Cl_2 + HSO_3F$$

The main products of the reactions of peroxydisulphuryl difluoride[79–82] and fluorine[83], chlorine[78], and bromine[82] fluorosulphates with nitrogen oxide, tetroxide, and pentoxide, as well as the reactions of peroxydisulphuryl difluoride with nitryl and nitrosyl chlorides[82] are nitryl and nitrosyl fluorosulphates, for example:

$$HalOSO_2F + N_2O_4 \rightarrow NO_2OSO_2F + HalNO_2$$

Hal=F, Cl;

$$(OSO_2F)_2 + 2ClNO_2 \rightarrow 2NO_2OSO_2F + Cl_2$$

Peroxydisulphuryl difluoride interacts vigorously with tetrafluorohydrazine[84,85]:

$$(OSO_2F)_2 + N_2F_4 \rightarrow 2F_2NOSO_2F$$

The substitution of halogen atoms in chlorosulphonic acid[86], chlorosulphonyl isocyanate[87], and phosphoryl bromide[88] or chloride[89] on treatment with chlorine fluorosulphate, bromine fluorosulphate, or peroxydisulphuryl difluoride yielded the corresponding fluorosulphates:

$$ClSO_2NCO + BrOSO_2F \xrightarrow{20^\circ} FSO_2OSO_2NCO$$

$$Br_3PO + (OSO_2F)_2 \rightarrow (FSO_2O)_3PO + Br(OSO_2F)_3$$

SO_2Cl_2,[89] SOClF,[55] and $SeOCl_2$[90] react analogously. The reaction with *N*-chlorosulphinylamine is more complex[91]:

$$ClNSO + ClOSO_2F \rightarrow Cl_2 + SO_2F_2 + SO(OSO_2F)_2 + N_2 + S_2O_5F_2 + SO_2 + ClN(SO_2F)_2 + Cl_2NSO_2F \ .$$

Chlorine[92,93] and bromine[94] fluorosulphates have been used to prepare chlorine and bromine perchlorates:

$$NO_2ClO_4 + BrOSO_2F \rightarrow BrOClO_3 \ .$$

Peroxydisulphuryl difluoride only oxidises phosphorus trifluoride, thionyl fluoride, and carbon monoxide[55,95,96], but adds to arsenic trifluoride[97], sulphur dioxide[5,55,98,99], and sulphur tetrafluoride[55,99]; in the presence of potassium fluoride, a mixed peroxide can be obtained from thionyl tetrafluoride[100]:

$$(OSO_2F)_2 \xrightarrow{AsF_3} AsF_3(OSO_2F)_2 \ ; \quad \xrightarrow{SO_2} F_2S_2O_6 \ ; \quad \xrightarrow{SF_4} F_4S(OSO_2F)_2 \ ; \quad \xrightarrow{OSF_4,\ KF} F_5SOOSO_2F \ .$$

The reactions with CO,[95,96] SO_2,[98,99] and SF_4[99] have been studied by kinetic methods.

Fluorine fluorosulphate[75,101–104] and (even at room temperature) chlorine fluorosulphate[78] readily combine with sulphur dioxide and carbon monoxide:

$$HalOSO_2F \xrightarrow{SO_2} HalSO_2OSO_2F \ ; \quad \xrightarrow{CO} HalCOOSO_2F \ ;$$

Hal F, Cl .

The kinetics of the reactions involving SO_2[101] and CO[103,104] have been investigated at 60–120 °C and 30–90 °C respectively.

Peroxydisulphuryl difluoride and fluorine fluorosulphate could not be made to add to difluorodiazine[105].

On interaction with peroxydisulphuryl difluoride, metal carbonyls form fluorosulphonate salts of different composition[55,106,107], for example:

$$W(CO)_6 + (OSO_2F)_2 \rightarrow WO(SO_3F)_4 \ .$$

Although the reagents considered belong to the class of the most vigorous oxidants, nevertheless a detailed study has been made of the possibility of increasing the oxidation state of the halogen atoms in halogen fluorosulphates. The interaction of peroxydisulphuryl difluoride with OF_2,[32,108] ClO_2,[109] I_2O_4 and I_2O_5,[110–112] $(SF_5O)_2$,[113] and $(SeF_5O)_2$[114] has also been investigated, for example:

$$(OSO_2F)_2 + (SF_5O)_2 \rightarrow 2SF_5OOSO_2F \ .$$

Chlorine (but not bromine) fluorosulphate readily interacts with ozone at 0 °C[115]:

$$ClOSO_2F + O_3 \rightarrow O_2ClOSO_2F \ .$$

Chlorine oxide difluoride has also been used to oxidise chlorine fluorosulphate[116]. Treatment of iodine fluorosulphate with chlorine and bromine yielded the fluorosulphates $IHal_2OSO_2F$ and $I_2HalOSO_2F$ (Hal = Cl or Br)[13,117]; the interaction of ICl_2OSO_2F and IBr_2OSO_2F leads to $IBrClOSO_2F$.[118]

The above main types of reactions of peroxydisulphuryl difluoride and halogen fluorosulphates (oxidation, introduction of the fluorosulphate group, or halogenation and addition to unsaturated compounds) are as a rule also characteristic of reactions with organic compounds.

III. METHODS OF SYNTHESIS OF PEROXYDISULPHURYL DIFLUORIDE AND HALOGEN FLUOROSULPHATES

Peroxydisulphuryl difluoride and halogen fluorosulphates have not as yet become readily available and widely used reagents but the methods of their synthesis have been developed and described in fair detail.

The historical aspects of the early methods of synthesis have been examined in other reviews[8,9], which also present data (partly supplemented in the review of Gillespie and Morton[119] and certain publications[27,120]) concerning related compounds containing the $Br_n^+SO_3F^-$ (n = 2,3) and $I_n^+SO_3F^-$ (n = 2–7) polycations.

The fluorination of sulphur trioxide with fluorine in the presence of silver difluoride still apparently remains the most suitable procedure for the synthesis of peroxydisulphuryl difluoride[121,122]:

$$SO_3 + F_2 \xrightarrow{AgF_2;\ 150°} (OSO_2F)_2 + FOSO_2F \ .$$

The reaction has been carried out repeatedly[1–4,48,55,100,121,123]; its main disadvantage is the possibility of the formation of the potentially dangerous fluorine fluorosulphate[48,122]. By varying the conditions, the latter can be isolated as the main product[2–4]. It has been recommended that small amounts of peroxydisulphuryl difluoride be obtained[9] at 170 °C under static conditions without a catalyst[100]. It is apparently more desirable to employ for this purpose the complex salt $CsAgF_4$[124]:

$$CsAgF_4 + SO_3 \xrightarrow{25°} (OSO_2F)_2 + CsAg(OSO_2F)_3 \ .$$

The methods of synthesis of peroxydisulphuryl difluoride by the electrolysis of fluorosulphonic acid in the presence of potassium fluorosulphate *in vacuo* at −23 °C (current yield 55%)[123], by the photochemical fluorination of sulphur trioxide with fluorine[125–127], and by the fluorination of copper or nickel fluorosulphates at 200 °C[123] are evidently not of preparative interest [with the exception of the generation of $(OSO_2F)_2$ *in situ*[52–54]]. The above photochemical reactions and the interaction of oxygen fluorides with sulphur trioxide[127–129] and particularly sulphur dioxide[128,130] lead to the formation not only of fluorine fluorosulphate but also of fluorine peroxyfluorosulphate $FOOSO_2F$. Fluorine fluorosulphate and sulphuryl fluoride have been obtained by the photochemical fluorination of $F_2S_2O_6$.[131]

Photochemical[108] or thermal[5,132] fluorination of peroxydisulphuryl difluoride leads to fluorine fluorosulphate whose treatment with sulphur trioxide at 90–300 °C[3,20,55] or with ultraviolet radiation[126,127,133] regenerates peroxydisulphuryl difluoride:

$$(OSO_2F)_2 \underset{+SO_3}{\overset{+F_2}{\rightleftharpoons}} 2FOSO_2F \ .$$

The fluorination of sulphur trioxide and fluorosulphonic acid with xenon fluorides[76,134–139], chromium pentafluoride[140], uranium hexfluoride[141,142], and trifluoromethyl hypofluorite[143], the decomposition of silver fluorosulphate[67], the reactions described above[75,76], and the oxidation of fluorosulphonic acid in accordance with the scheme[144]

$$HSO_3F + O_2^+[AsF_6]^- \rightarrow (OSO_2F)_2$$

are fairly exotic methods of synthesis of peroxydisulphuryl difluoride.

Very pure fluorine fluorosulphate is formed on decomposition of tetrafluoroammonium fluorosulphate[145]:

$$NF_4OSO_2F \xrightarrow{10°} NF_3 + FOSO_2F \ .$$

Chlorine, bromine, and iodine fluorosulphates are obtained by treating peroxydisulphuryl difluoride with the corresponding halogens:

$$(OSO_2F)_2 + Hal_2 \rightarrow 2HalOSO_2F \ ; \quad Hal=Cl, Br, I \ .$$

The reaction with chlorine requires fairly severe conditions—the mixture of reactants must be heated in an autoclave for 5 days at 125 °C[7]; the process kinetics have been investigated[21]. It has been shown comparatively recently with the aid of spectra that, in solution in fluorosulphonic acid, chlorine interacts with $(OSO_2F)_2$ even at room temperature[146]. Bromine[6,12] and iodine[6,13,119] react at 25 °C and, depending on the molar ratios, it is possible to obtain either mono or tris-fluorosulphates of bromine or iodine:

$$(OSO_2F)_2 + Br_2 \rightarrow BrOSO_2F \underset{+Br_2}{\overset{+(OSO_2F)_2}{\rightleftharpoons}} Br(OSO_2F)_3 \ .$$

It follows from the foregoing that in the general case the ease of synthesis of halogen fluorosulphates is determined by the availability of peroxydisulphuryl difluoride. It is of interest to note that the interaction of iodine monochloride with peroxydisulphuryl difluoride leads to iodine trisfluorosulphate[55]:

$$ICl + (OSO_2F)_2 \rightarrow I(OSO_2F)_3 + Cl_2 \ .$$

Another pathway leading to the formation of the above reagents is based on the synthesis of chlorine fluorosulphate by the addition of chlorine monofluoride to sulphur trioxide[11,35,147,148]:

$$ClF + SO_3 \rightarrow ClOSO_2F \ .$$

The initial substances are condensed at −196 °C and are slowly heated to room temperature[11,35,148]. Ultraviolet irradiation of the chlorine fluorosulphate formed in almost quantitative yield gives rise to peroxydisulphuryl difluoride (yield 94–97%)[11,149] and treatment with bromine produces bromine fluorosulphate in 93% yield[148]:

$$ClOSO_2F \begin{cases} \xrightarrow{h\nu} (OSO_2F)_2 + Cl_2 \ ; \\ \xrightarrow{Br_2} BrOSO_2F \ . \end{cases}$$

The report of the possible formation of chlorine fluorosulphate in the reaction of nitryl chloride with the anhydride of fluorosulphonic acid[150] has not been reliably confirmed.

Thus the methods of synthesis of peroxydisulphuryl difluoride and halogen fluorosulphates are not complex and these substances can be readily obtained in any laboratory where studies with fluorine or fluorides are prosecuted.

IV. SUBSTITUTION OF HYDROGEN AND HALOGEN ATOMS AND CERTAIN FUNCTIONAL GROUPS

In view of the highly corrosive nature of peroxydisulphuryl difluoride and halogen fluorosulphates, the study of their reactions with organic compounds was begun in relation to the fully halogenated derivatives. Already at the beginning of the 1960's, it was shown that both peroxydisulphuryl difluoride[55] and bromine[6,12] and iodine[13] fluorosulphates react vigorously with carbon tetrachloride at room temperature to form phosgene:

$$CCl_4 \begin{cases} \xrightarrow{(OSO_2F)_2} COCl_2 + O(SO_2F)_2 + Cl_2 \ ; \\ \xrightarrow{2BrOSO_2F} COCl_2 + O(SO_2F)_2 + 2BrCl \ . \end{cases}$$

The above reactions can be regarded formally as direct oxidation, but one cannot rule out the possibility also of the intermediate formation and then decomposition of bis(fluorosulphato)dichloromethane. The latter hypothesis was soon confirmed and, depending on the reactant ratio, mono-, bis-, tris-, and tetrakis-(fluorosulphato)methanes were obtained at −22 °C[89]:

$$CCl_4 \xrightarrow[-BrCl]{+BrOSO_2F} CCl_n(OSO_2F)_{4-n} \ ; \quad n = 0-3$$

The second chlorine atom in carbon tetrachloride is apparently somewhat more readily substituted by the fluorosulphato-group using bromine fluorosulphate, since bis-(fluorosulphato)dichloromethane is formed together with the mono(fluorosulphato)-derivative even in the presence of a fivefold excess of carbon tetrachloride[89].

Further study of the reactivity of the above reagents showed that substitution by the fluorosulphato-group of the hydrogen atoms in alkanes, including hydrogen-containing polychlorofluoroalkanes but not bromoalkanes, and also in the OH, NH, NH_2, and similar groups is most characteristic of peroxydisulphuryl difluoride. Chlorine and bromine fluorosulphates are more effective for the substitution of halogen atoms (sometimes even fluorine atoms) by the fluorosulphato-group. The chlorinating (brominating) effect of these fluorosulphates in reactions with alkanes is not usually manifested, but this rule does not extend to functional groups and aromatic compounds.

Here one must bear in mind that the fluorosulphonic acid formed on substitution of hydrogen atoms by peroxydisulphuryl difluoride frequently tends to cause the degradation of the reaction products. On the other hand, the substitution of halogen atoms on treatment with chlorine and bromine fluorosulphates is accompanied by the liberation of the corresponding halogen or mixed halogen, which can be removed much more readily.

Next we shall consider the interactions of peroxydisulphuryl difluoride and then of the halogen fluorosulphates with various bonds and groups.

A. Aliphatic Compounds

1. Substitution of Hydrogen Atoms in Alkanes and Substituted Alkanes

Peroxydisulphuryl difluoride successfully substitutes the hydrogen atom in methylene chloride by the fluorosulphato-group even at −25 °C[77]. The attempt to substitute the second hydrogen atom was unsuccessful and only phosgene was isolated, in contrast to the interaction with methyl fluorosulphate, where bis(fluorosulphato)methane is formed smoothly and with a high yield[77]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CH_2Cl_2} CHCl_2OSO_2F \xrightarrow{(OSO_2F)_2} COCl_2 \ ; \\ \xrightarrow{CH_3OSO_2F} CH_2(OSO_2F)_2 \ . \end{cases}$$

The reaction with methylene chloride has been carried out in trichlorofluoromethane; in the absence of the latter, vigorous explosions were observed.

Fairly unambiguous results are apparently achieved when peroxydisulphuryl difluoride is used at the instant of formation in electrolysis. Thus, by bubbling methane into the anodic compartment of the electrolytic cell containing a 1 M solution of potassium fluorosulphate in fluorosulphonic acid, it is possible to obtain selectively methyl fluorosulphate (yield 1–61%) or bis(fluorosulphato)methane (yield 6–63%), depending on the current density, temperature, and the degree of dispersion of the gas streams[52–54]:

$$CH_4 \xrightarrow[KSO_3F/HSO_3F]{(OSO_2F)_2} CH_3OSO_2F + CH_2(OSO_2F)_2 \ .$$

Analogous results have been obtained also for ethane[52,53]. The process kinetics have been investigated[54], suggesting a radical reaction mechanism.

Under these conditions, acetone is cleaved, bis(fluorosulphato)methane is formed from acetic acid, and in propionic acid the hydrogen atom in the β-position is substituted by the fluorosulphato-group, which leads to the relatively unstable β-fluorosulphatopropionic acid[52]:

$$(OSO_2F)_2 \mid KSO_3F/HSO_3F \mid \begin{cases} \xrightarrow{(CH_3)_2CO} MeOSO_2F + CH_2(OSO_2F)_2 + CH_3C(O)OSO_2F \\ \xrightarrow{C_2H_5COOH} FSO_2OCH_2CH_2COOH \xrightarrow[-HSO_3F]{-25^\circ} CH_2{=}CHCOOH \end{cases}$$

It was shown for the first time in 1972[151] that peroxydisulphuryl difluoride is effective even in relation to the primary hydrogen atoms in monohydrochloro- fluoro- and monohydroperfluoro-alkanes, which are exceptionally inert as regards radical substitution[77,151]. The reaction has been achieved with dichlorofluoro- and trifluoro-methanes, monohydroperfluoroethane[77], and monohydroperfluoropropane[151] at room temperature or with heating to 40–50 °C, for example:

$$CF_3(CF_2)_2H + (OSO_2F)_2 \rightarrow CF_3(CF_2)_2OSO_2F + HSO_3F .$$

The secondary hydrogen atoms in 2-chloro-2-hydro- and 2-hydroperfluoro-propanes are substituted even more readily (at 5–10 °C) by the fluorosulphato-group, but only hexafluoroacetone has been obtained from 2,2-dihydrohexafluoropropane[152]:

$$(CF_3)_2CH_2 + (OSO_2F)_2 \rightarrow (CF_3)_2CO .$$

The selectivity of the action of peroxydisulphuryl difluoride in relation to the hydrogen atom is indicated by the successful substitution of the latter in difluoronitromethane[153], α-hydroperfluoropropionitrile[152], ω-hydroperfluoroheptanonitrile[151], and 1-hydrotetrafluoroethylsulphur pentafluoride and 2-hydrohexafluoro-2-propylsulphur pentafluoride[154]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{O_2NCF_2H} O_2NCF_2OSO_2F \\ \xrightarrow{H(CF_2)_6CN} FSO_2O(CF_2)_6CN \\ \xrightarrow{(CF_3)_2CHSF_5} (CF_3)_2C(SF_5)OSO_2F \end{cases}$$

Treatment of 2,2,2-trifluoroethylsulphur pentafluoride with two moles of peroxydisulphuryl difluoride led only to trifluoroacetyl fluoride[154]:

$$CF_3CH_2SF_5 + (OSO_2F)_2 \rightarrow CF_3C(=O)F .$$

There is no doubt about the radical nature of the reactions considered, but no examples of the dimerisation of the hydrocarbon radicals formed as a result of the abstraction of a hydrogen atom by the fluorosulphate radical have been noted.

According to the authors[151], they obtained proof that such radicals really exist by treating a film of the vinylidene fluoride–perfluoropropene copolymer with gaseous peroxydisulphuryl difluoride at 50 °C, which makes it possible to introduce into the specimen a fairly large number of fluorosulphato-groups (the sulphur content was 7.21%). Even after the removal of these groups by treatment with aqueous pyridine, the polymer remained rigid and insoluble in acetonitrile, which is explained by its "cross-linked" nature[151].

Peroxydisulphuryl difluoride also readily interacts with the potassium salts of bromodinitromethane[153] and dinitroacetonitrile[100]. A radical-ion reaction mechanism has been put forward[100]:

$$\dot{O}SO_2F + [NCC(NO_2)_2]^- \xrightleftharpoons{-SO_2F^-} [NCC(NO_2)_2]^{\cdot} \xrightarrow{\dot{O}SO_2F} NCC(NO_2)_2OSO_2F .$$

As mentioned above, halogen fluorosulphates are inert with respect to the CH bond at the usual temperatures but vigorously substitute halogens. The only exception is apparently fluorine fluorosulphate, which reacts with chloroform in the gas phase even at −78 °C to form dichloromethyl fluorosulphate (80%) and trichlorofluoromethane (13%)[155]:

$$FOSO_2F + CHCl_3 \rightarrow CHCl_2OSO_2F + CFCl_3 .$$

Although in the main the process is directed towards the substitution of a halogen atom, the substitution of a hydrogen atom by fluorine under these conditions cannot in all probability be accounted for by the effect of chlorine monofluoride.

Chlorine fluorosulphate has been used successfully to chlorinate nitroform and dinitroacetonitrile salts[153]:

$$ClOSO_2F + KC(NO_2)_3 \rightarrow ClC(NO_2)_3 .$$

2. Substitution of Halogen Atoms in Halogenoalkanes and Carboxylic and Sulphonic Acid Chlorides

In contrast to the reactions discussed above, peroxydisulphuryl difluoride substitutes selectively the bromine atoms in methyl bromide[77] and in 1-bromopropane[156] by the fluorosulphato-group at room or a reduced temperature:

$$(OSO_2F)_2 + CH_3Br \rightarrow CH_3OSO_2F + BrOSO_2F + Br_2 .$$

In all probability, in this case peroxydisulphuryl difluoride substitutes bromine atoms only in the first instants, since the bromine fluorosulphate formed is much more reactive in the process. The bromine evolved readily interacts with peroxydisulphuryl difluoride, generating bromine fluorosulphate. These factors explain both the selectivity of the above reactions and the ease of substitution of the bromine atoms in other bromine-containing compounds.

Thus peroxydisulphuryl difluoride successfully substitutes the bromine atoms in bromotrifluoro-[157], dibromodifluoro-, tribromofluoro-, and tetrabromo-methanes[158]. In the last two examples carbonyl compounds are formed, including the relatively unstable carbonyl bisfluorosulphate[158]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CBr_3F} FC(OSO_2F)_3 + FC(O)OSO_2F \\ \xrightarrow{CBr_4} OC(OSO_2F)_2 + CO_2 + S_2O_5F_2 \end{cases}$$

The reaction has also been extended to bromotris(difluoroamino)methane[159], 3-bromoheptafluoro-2-butanone[160], and trifluoroacetyl bromide[161]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{(F_2N)_3CBr} (F_2N)_3COSO_2F \\ \xrightarrow{CF_3C(O)CFBrCF_3} CF_3C(O)CF(CF_3)OSO_2F \\ \xrightarrow{CF_3C(O)Br} CF_3C(O)OSO_2F + CF_3OSO_2F \end{cases}$$

Chlorine atoms are substituted by peroxydisulphuryl difluoride with much more difficulty. As mentioned above, the only compounds which react under comparatively mild conditions are carbon tetrachloride (phosgene is formed at 25 °C[55]) and trichlorofluoromethane (20 days, 40 °C[142]). The chlorine atom in chlorotrifluoromethane could be substituted by the fluorosulphato-group only by heating the reactants at 150 °C and a pressure of 304×10^5 N m^{-2} for five days[157]. It has been shown spectroscopically[146] that 1,1,2-trichlorotrifluoroethane also reacts at 150 °C and only in the presence of fluorosulphonic acid. Peroxydisulphuryl difluoride substitutes the difluoroamino-group in difluoroaminocarbonyl chloride[162]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CCl_3F} CCl_2FOSO_2F \\ \xrightarrow[HSO_3F]{CClF_2CCl_2F} CClF_2CClFOSO_2F \\ \xrightarrow{ClC(O)NF_2} ClC(O)OSO_2F + F_2NOSO_2F \end{cases}$$

The single example of the substitution of the chlorine atom in chloroform by fluorine fluorosulphate was described above[155].

Chlorine fluorosulphate has been used successfully even at temperatures below 0 °C to synthesise chloromethyl and chloroethyl fluorosulphates from methylene chloride and dichloroethane[86,163]. Treatment of *sym*-tetrachloroethane with two moles of chlorine fluorosulphate leads to a mixture of 1,1- and 1,2-bis(fluorosulphato)dichloroethanes in proportions of 3:1[164]:

$$ClOSO_2F \xrightarrow{ClCH_2CH_2Cl} ClCH_2CH_2OSO_2F \ ;$$
$$ClOSO_2F \xrightarrow{Cl_2CHCHCl_2} Cl_2CHCH(OSO_2F)_2 + FSO_2OCHClCHClOSO_2F \ .$$

At −40 °C chlorine fluorosulphate substitutes selectively the chlorine atom in alkyl monochloroacetates by the fluorosulphato-group[86,163]:

$$ClOSO_2F + ClCH_2COOR \rightarrow FSO_2OCH_2COOR \ .$$

The esters of fluorosulphatoacetic acid formed are relatively unstable at room temperature but, by virtue of their high reactivity, can be used *in situ* in further syntheses[86].

In the presence of fluorosulphonic acid, chlorine fluorosulphate substitutes vigorously the first chlorine atom in 1,1,2-trichlorotrifluoroethane by the fluorosulphato-group even at room temperature (with a small exothermic heat change)[165]:

$$CClF_2CCl_2F + ClOSO_2F \rightarrow CClF_2CClFOSO_2F + Cl_2 \ .$$

This indicates a much greater effectiveness of chlorine fluorosulphate in relation to the C–Hal bonds compared with peroxydisulphuryl difluoride, since the latter undergoes an analogous reaction only at 150 °C.[146]

Dichlorodifluoromethane and *sym*-tetrachlorodifluoroethane react analogously; at 70–85 °C it is possible to substitute two or three chlorine atoms in these compounds, while at 120 °C all the chlorine atoms and one fluorine atom are substituted in *sym*-tetrachlorodifluoroethane[146,165]:

$$ClOSO_2F \xrightarrow{CClF_2CCl_2F,\ 85°} CClF_2CF(OSO_2F)_2 \ ;$$
$$ClOSO_2F \xrightarrow{CCl_2FCCl_2F,\ 85°} FSO_2OCClFCF(OSO_2F)_2 \xrightarrow[120°]{ClOSO_2F} (FSO_2O)_2CFC(O)OSO_2F \ .$$

It must be emphasised that the substitution takes place smoothly only in the presence of fluorosulphonic acid, the employment of which as the solvent tends to reduce the reaction temperature[146,165].

The role of fluorosulphonic acid† apparently reduces to enhancing the polarisation of the chlorine atom in chlorine fluorosulphate. A study of ^{19}F NMR spectra showed that, after mixing in equimolar proportions, the individual signals of chlorine fluorosulphate (−112.2 p.p.m. relative to CF_3COOH) and fluorosulphonic acid (−119 p.p.m.) disappear and a single signal (broadened singlet) appears at −116.1 p.p.m.[86] An equimolar mixture of chlorine fluorosulphate and fluorosulphonic acid can be separated into its components almost quantitatively by fractionation[86]. It may be that the halogen is substituted via a one-electron transfer mechanism[86]:

$$Cl{-}O{-}SO_2F + H^+ + SO_3F^- \rightarrow Cl{-}\overset{+}{O}(H){-}SO_2F + SO_3F^- \ ;$$

$$R{:}{\rightarrow}Cl + Cl{:}\overset{\delta+}{O}(H){-}SO_2F \rightarrow \dot{R} + \cdot\overset{+}{O}(H){-}SO_2F + Cl_2$$

$$ROSO_2F \xleftarrow[-HSO_3F]{SO_3F^-} R{-}\overset{+}{O}(H){-}SO_2F \ .$$

Subsequently it was shown that the reactivity of chlorine fluorosulphate increases significantly also after the addition of bromine[166,167]. This involves the substitution of the primary chlorine atom in chloropentafluoroethane and 1,2-dichlorohexafluoropropane sulphato-group, while in 1,2-dichlorotetrafluoroethane one or both chlorine atoms are substituted depending on the conditions[167]:

$$ClOSO_2F + ClCF_2CF_2Cl \xrightarrow[130°,\ 5\ days]{Br_2} ClCF_2CF_2OSO_2F \xrightarrow[140°,\ 14\ days]{ClOSO_2F,\ Br_2} FSO_2OCF_2CF_2OSO_2F \ .$$

Without the addition of bromine, the chlorine atoms in these compounds are not substituted either by peroxydisulphuryl difluoride or chlorine fluorosulphate[166,167]. The authors naturally explained the effectiveness of bromine by the formation of bromine fluorosulphate *in situ* (cf. Schack and Wilson[148]) and its subsequent regeneration during the reaction.

The chlorine atoms in 2-chlorotetrafluoroethyltrifluoromethyl ether[166] and, with catalysis by fluorosulphonic acid, in chlorocarbonyl fluorosulphate[146] and C_2–C_9 perfluoroacyl chlorides[86,168] have also been substituted by the fluorosulphato-group following the addition of bromine:

$$ClOSO_2F \xrightarrow{CF_3OCF_2CF_2Cl,\ Br_2,\ 110°} CF_3OCF_2CF_2OSO_2F + Cl_2 \ ;$$
$$ClOSO_2F \xrightarrow[30°]{ClC(O)OSO_2F,\ HSO_3F} S_2O_5F_2 + CO_2 + Cl_2 \ :$$
$$ClOSO_2F \xrightarrow[20-60°]{CF_3C(O)Cl,\ HSO_3F} CF_3C(O)OSO_2F + Cl_2 \ .$$

The fluorides of perfluorocarboxylic acids are much less reactive and the mixed anhydride of perfluoropelargonic and fluorosulphonic acid has been obtained in only a low yield by heating the corresponding acid fluoride with chlorine fluorosulphate (28 h at 80 °C), the reaction being catalysed by fluorosulphonic acid[86].

As was to be expected, the bromine atom in bromoperfluoroalkanes reacts with chlorine fluorosulphate more readily than the chlorine atom. The primary bromine atoms in perfluorinated bromo- and 1,2-dibromoethanes and also in 1,2- and 1,3-dibromopropanes are substituted at 25 °C (after 21–24 days); at 50–65 °C both primary bromine atoms of dibromoperfluoroalkanes react[167]:

$$ClOSO_2F \xrightarrow[65°,\ 2\ days]{BrCF_2CF_2Br,} \underset{64\%}{FSO_2OCF_2CF_2OSO_2F} + \underset{31\%}{ClCF_2CF_2OSO_2F} \ ;$$
$$ClOSO_2F \xrightarrow[50°,\ 11\ days]{Br(CF_2)_3Br,} \underset{57\%}{FSO_2O(CF_2)_3OSO_2F} + \underset{10\%}{Cl(CF_2)_3OSO_2F} \ .$$

The secondary bromine atoms in 1,2-dibromo- and 2-bromoperfluoro-propanes are not substituted under these conditions[167].

As mentioned above, bromine fluorosulphate substitutes by perfluorosulphato-groups all the chlorine atoms in carbon tetrachloride[89]. Mixtures of mono- and bis-(fluorosulphato)-derivatives are formed from trichlorofluoromethane at −55 °C and from oxalyl chloride at −2 °C.[89] Chlorocarbonyl

† Chlorosulphonic acid interacts with chlorine fluorosulphate and is converted into fluorosulphonic acid[86].

fluorosulphate has been obtained by the reaction of bromine fluorosulphate with a sevenfold excess of phosgene at −65 °C, but only the difluoroamino-group is substituted in difluoroaminocarbonyl chloride[162]:

$$BrOSO_2F \xrightarrow{CCl_3F} CCl_2FOSO_2F + CClF(OSO_2F)_2 \ ;$$
$$BrOSO_2F \xrightarrow{ClC(O)C(O)Cl} ClC(O)C(O)OSO_2F + FSO_2OC(O)C(O)OSO_2F \ ;$$
$$BrOSO_2F \xrightarrow{ClC(O)NF_2} ClC(O)OSO_2F + N_2F_4 \ .$$

The above facts clearly show that bromine fluorosulphate is more reactive towards the C—Cl bond than not only peroxydisulphuryl difluoride but also chlorine fluorosulphate.

In conclusion, one should note that bromine fluorosulphate has been used successfully to substitute the chlorine atoms in methanesulphonyl[169] and trifluoromethanesulphonyl chlorides[170] by the fluorosulphato-group. Methanesulphonyl fluorosulphate proved to be metastable; at 80 °C it decomposes into methanesulphonyl fluoride and sulphur trioxide[169]:

$$BrOSO_2F \xrightarrow{CH_3SO_2Cl} CH_3SO_2OSO_2F \xrightarrow{80^\circ} CH_3SO_2F + SO_3 \ ;$$
$$BrOSO_2F \xrightarrow{CF_3SO_2Cl} CF_3SO_2OSO_2F \ .$$

3. *Reactions with Alcohols and Carboxylic Acids*

The reactions of peroxydisulphuryl difluoride with alcohols have attracted the attention of investigators as possible ways of synthesising organic peroxides and mixed peroxides (of the type of ROOSO$_2$F), the potential initiators of radical

The yield of fluorosulphuryl trifluoromethyl peroxide does not exceed 50%, since in the presence of potassium and particularly caesium fluoride it can decompose approximately under the conditions of its synthesis[100]:

$$CsF + CF_3OOSO_2F \xrightarrow{25^\circ,\ 2\ h} CsOCF_3 + SO_2F_2 + O_2 \ .$$

Fluorosulphuryl perfluoroisopropyl peroxide decomposes during storage in glass vessels at room temperature[100], while fluorosulphonyl perfluoro-t-butyl peroxide decomposes only on heating to 100 °C[173]:

$$(CF_3)_3COOSO_2F \rightarrow CF_3OSO_2F + (CF_3)_2CO \ .$$

The above facts show that the radical-ion mechanism proposed[100] for the reactions of peroxydisulphuryl difluoride with anions is apparently not fully justified at least for perfluoroalkyl alkoxides. This can be seen particularly clearly in relation to perfluoro-t-alkyl alcohols and the corresponding alkoxides. Not even traces of the mixed peroxide or the corresponding perfluoro-t-alkoxy-radicals could be detected in reactions with alcohols[77] as a consequence of the ready decomposition of the perfluoro-t-alkoxy-radical via the mechanism

$$C_2F_5C(CF_3)_2OH + \dot{O}SO_2F \rightarrow C_2F_5C(CF_3)_2\dot{O} + HSO_3F \ ;$$
$$C_2F_5C(CF_3)_2\dot{O} \rightarrow (CF_3)_2CO + \dot{C}F_5 \ ;$$
$$C_2F_5C(CF_3)_2\dot{O} \rightarrow C_2F_5C(O)CF_3 + \dot{C}F_3 \ ;$$
$$\dot{C}F_5 + (OSO_2F)_2 \rightarrow C_2F_5OSO_2F + \dot{O}SO_2F \ ;$$
$$\dot{C}F_3 + (OSO_2F)_2 \rightarrow CF_3OSO_2F + \dot{O}SO_2F \ .$$

All the final compounds presented in the above scheme have been identified; perfluoroethyl fluorosulphate and trifluoro-

Bearing in mind that only trifluoromethyl fluorosulphate is formed also in the reaction of peroxydisulphuryl difluoride with sodium trifluoroacetate[100], it is apparently hardly possible to expect an acceptable stability of fluorosulphuryl trifluoroacetyl peroxide even if the latter is formed under these conditions.

The reactions of chlorine and bromine fluorosulphates with alcohols and carboxylic acids began to be investigated only recently. The interaction of chlorine fluorosulphate with polyfluoroalcohols in dichlorodifluoromethane or 1,1,2-trichlorotrifluoroethane at −30°– −15 °C leads to the corresponding hypochlorites[175]:

$$ClOSO_2F + RCH_2OH \rightarrow RCH_2OCl + HSO_3F \ ;$$
$$R = H(CF_2)_n,\ O_2NCF_2;\ n = 2, 4, 6 \ .$$

The yield of hypochlorites does not exceed 40%, apparently as a consequence of decomposition under the influence of fluorosulphonic acid and the acid sulphates formed from the corresponding alcohols as side products. In the absence of water and acid impurities, such hypochlorites are fairly stable, particularly higher hypochlorites[175]. However, treatment of 2,2-dinitropropanediol with chlorine fluorosulphate led to the isolation of only dichlorodinitromethane in a low yield[153].

It has been noted[176] that chlorine fluorosulphate chlorinates trifluoro- and chlorodifluoro-acetic acids as well as their salts more effectively than chlorine monofluoride at temperatures between −78° and −45 °C. The hypochlorites of these acids are volatile and tend to decompose with detonation even at a pressure of the pure substance in a vacuum system of ~ 40 mmHg; they have been fairly fully characterised[176] and have been used successfully *in situ* for the synthesis (at −78 °C) of chloroperfluoro-esters[176,177] and perfluoroalkyl halides[167,178]. Perfluorodicarboxylic acids have also been introduced into the latter reaction[167,178]. Bromine fluorosulphate reacts similarly[167,178]:

$$ClOSO_2F \xrightarrow{CF_3COOH} CF_3CC(O)OCl \begin{cases} \xrightarrow{CF_2=CFCF_3} CF_3COOCF_2CClFCF_3 \ ; \\ \xrightarrow{25°} CF_3Cl \ ; \end{cases}$$
$$ClOSO_2F + CF_2(CF_2COOH)_2 \rightarrow Cl(CF_2)_3Cl + Cl(CF_2)_2COF + Cl(CF_2)_3OSO_2F \ ;$$
$$BrOSO_2F + C_2F_5COONa \rightarrow C_2F_5Br \ .$$

4. *Reactions with Peroxides, Ethers, Carboxylic Acid Anhydrides, and Certain Other Compounds*

Peroxydisulphuryl difluoride is inert with respect to perfluoroalkyl ethers up to 140 °C[166] and does not interact with perfluoroepoxypropane[151].

Bis(trifluoromethyl) peroxide reacts with peroxydisulphuryl difluoride only at fairly high temperatures (up to 240 °C)[179, 180], forming the corresponding mixed peroxide; the process kinetics have been studied in the range 185–230 °C[179]. The same peroxide has been obtained from bis(trifluoromethyl) trioxide in a yield of 87% at a temperature as low as 75 °C[181]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CF_3OOCF_3} CF_3OOSO_2F \ ; \\ \xrightarrow{CF_3OOOCF_3} CF_3OOSO_2F \ . \end{cases}$$

The reaction involving difluorophosphoryl trifluoromethyl peroxide CF_3OOPOF_2 at room temperature was found to entail only a slow decomposition to COF_2, POF_3, etc.[182]

The anhydrides of perfluorinated mono- and di-carboxylic acids react with peroxydisulphuryl difluoride slowly at 25 °C and rapidly at 100 °C, forming mixed anhydrides of fluorosulphonic and carboxylic acids and also perfluoroalkyl fluorosulphates, which, together with carbon dioxide, are apparently the products of the decomposition of the mixed peroxides of fluorosulphonic and carboxylic acids[183]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{(CF_3CO)_2O} CF_3COOSO_2F + CF_3OSO_2F + CO_2 \ ; \\ \xrightarrow{OCOCF_2CF_2CO} FSO_2OCF_2CF_2COOSO_2F + CO_2 \ . \end{cases}$$

In another study[184] only fluoroalkyl fluorosulphates were isolated in an analogous reaction; in this case difluoromethyl fluorosulphate was obtained from difluoroacetic acid anhydride with retention of the hydrogen atom.

Chlorine fluorosulphate and trifluoroacetic anhydride give rise to a mixed anhydride (yield 80–85%) and chlorotrifluoromethane[167]:

$$ClOSO_2F + (CF_3CO)_2O \rightarrow CF_3COOSO_2F + CClF_3 + CO_2 \ .$$

Other reactions accompanied by the rupture of carbon–carbon bonds include the interaction between peroxydisulphuryl difluoride and oxalyl chloride[162] and also the substitution of the cyano-group in ethyl cyanodinitroacetate by a chlorine atom on treatment with chlorine fluorosulphate at temperatures between −20° and −30 °C[153]:

$$(OSO_2F)_2 + ClC(O)C(O)Cl \rightarrow ClCOOSO_2F \ ;$$
$$ClOSO_2F + NCC(NO_2)_2COOC_2H_5 \rightarrow ClC(NO_2)_2COOC_2H_5 \ .$$

Dichlorodinitromethane has been obtained in a low yield from ethyl chlorodinitroacetate on treatment with $ClOSO_2F$.[153]

In addition it has been shown that peroxydisulphuryl difluoride readily substitutes the methyl groups in organotin compounds[185]:

$$(OSO_2F)_2 + (CH_3)_4Sn \rightarrow (CH_3)_2Sn(OSO_2F)_2 + (CH_3)_3SnOSO_2F \ .$$

5. *Substitution of Hydrogen or Halogen Atoms in Amines, Imines, Halogenoimines, and Carboxylic Acid Amides*

Peroxydisulphuryl difluoride smoothly substitutes the hydrogen atom in bis(trifluoromethyl)amine by the fluorosulphato-group[77]. Hexafluoroacetone imine reacts in a more complex manner; together with substitution, the imine undergoes oxidative dimerisation and peroxydisulphuryl difluoride apparently adds to the resulting diazadiene[77]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{(CF_3)_2NH} (CF_3)_2NOSO_2F \ ; \\ \xrightarrow{(CF_3)_2C=NH} (CF_3)_2CNOSO_2F + (CF_3)_2CNN=C(CF_3)_2 + \\ \quad + FSO_2OC(CF_3)_2N=NC(CF_3)_2OSO_2F \ . \end{cases}$$

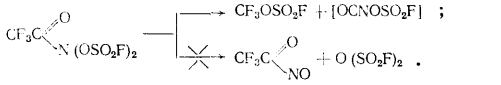
The reactions take place at temperatures as low as 0–25 °C and are clearly of a radical type. In contrast to this, the sodium salt of fluorosulphurylcarbamoyl fluoride reacts slowly with peroxydisulphuryl difluoride only at 70 °C and the yield of the final product is only 17%[186]:

$$(OSO_2F)_2 + Na^+[FSO_2NCOF]^- \rightarrow FSO_2N(OSO_2F)COF \ .$$

The reaction of peroxydisulphuryl difluoride with perfluorocarboxylic acid amides is extremely unusual[187]. In the presence of $(OSO_2F)_2$ a suspension of the initial amide in 1,1,2-trichlorotrifluoroethane dissolves fully at temperatures as low as −30– −25 °C, but fluorosulphonic acid precipitates from solution only after several hours, usually after the temperature of the mixture approaches room temperature[187]:

$$RC(O)NH_2 + 2(OSO_2F)_2 \rightarrow RC(O)N(OSO_2F)_2 + 2HSO_3F \ ;$$
$$R = CF_3,\ C_3F_7,\ C_6F_{13} \ .$$

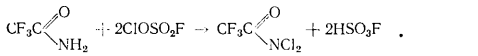
Although the amount of the fluorosulphonic acid formed is consistent with stoichiometry, *N*,*N*-bis(fluorosulphato)amides have been obtained in yields less than 25%, because, under the conditions of the synthesis and on isolation, they decompose into perfluoroalkyl fluorosulphate and possibly fluorosulphatoisocyanate. The expected perfluoroacylnitroso-compounds and pyrosulphuryl difluorides could not be isolated in this reaction[187]:



Chlorine and bromine fluorosulphates have been used successfully even at reduced temperatures to substitute fluorine[187] and chlorine[77] atoms respectively in hexafluoroacetone *N*-halogenoimines by the fluorosulphato-group, for example:

$$ClOSO_2F + (CF_3)_2C{=}NF \rightarrow (CF_3)_2C{=}NOSO_2F \ .$$

Also at reduced temperatures, chlorine fluorosulphate vigorously substitutes the hydrogen atoms in the amides of trifluoroacetic and heptafluorobutyric acids by chlorine:



However, the yields of *N*,*N*-dichloroamides are low, possibly as a consequence of the formation of fluorosulphonic acid[163,189].

B. Aromatic Compounds

As early as 1971, Merrill reported[156] at the VIth International Symposium on the Chemistry of Fluorine that a hydrogen atom in benzene can be substituted by the fluorosulphato-group on treatment with peroxydisulphuryl difluoride in trichlorofluoromethane at −45 °C:

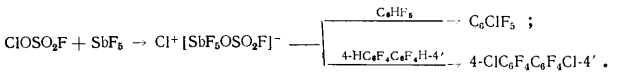
$$(OSO_2F)_2 + C_6H_6 \rightarrow C_6H_5OSO_2F \ .$$

Toluene, which is substituted in the ring, reacts even more vigorously, but the position of the fluorosulphato-group relative to the methyl group has not been established[77].

Chlorine fluorosulphate proved to be a unique chlorinating agent for benzene. At a temperature as low as −100 °C and for the molar ratio $ClOSO_2F:C_6H_6 = 1:1.5$, hexachlorobenzene was obtained unexpectedly in a yield of ~ 80%[190]:

$$ClOSO_2F + C_6H_6 \rightarrow C_6Cl_6 \ .$$

The complex of chlorine fluorosulphate with antimony pentafluoride has been used successfully to chlorinate pentafluorobenzene and octafluorobiphenyl[191]:

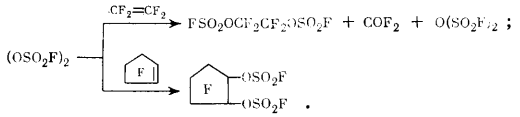


Iodine fluorosulphate interacts vigorously with pyridine, but the yellow solid formed decomposes rapidly and is converted into a brown oil, whose structure has not been established[13].

V. ADDITION OF PEROXYDISULPHURYL DIFLUORIDE AND HALOGEN FLUOROSULPHATES TO UNSATURATED COMPOUNDS

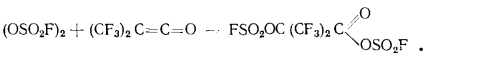
1. Addition to Carbon–Carbon Multiple Bonds

The addition of peroxydisulphuryl difluoride to carbon–carbon double bonds was achieved for the first time in 1961 in relation to tetrafluoroethylene and perfluorocyclopentene[55]:

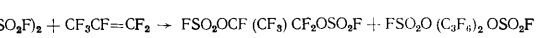


The olefin, diluted with nitrogen, was added slowly *in vacuo* (~ 125 mmHg) to peroxydisulphuryl difluoride. A slight increase of the rate of supply of tetrafluoroethylene led to a rapid increase of temperature and the formation of a brown gas in the reactor, which, according to the authors[55], might have indicated the appearance of free radicals. At the same time the appearance of a solid white powder in the gas connections and on the walls of the vessel was observed; up to 5% of tetrafluoroethylene was oxidised to carbonyl fluoride[55].

Subsequently the corresponding vicinal bis(fluorosulphato)-polyfluoroalkanes were obtained from chlorotrifluoroethylene[157], perfluoropropene[151,192], perfluorobutene[157,192,193], perfluorocyclobutene[192], 1,2-dichlorohexafluorocyclopentene[151], and perfluoro-derivatives of pent-2-ene and hex-2-enes[193]. Peroxydisulphuryl difluoride adds just as readily to trichloroethylene (the hydrogen atom is not then substituted)[156] and also to bis(trifluoromethyl)keten[194]:



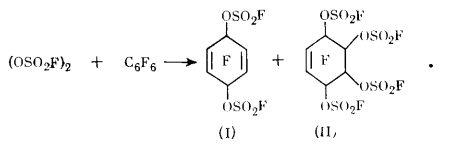
The above reactions were as a rule carried out at room temperature and, more rarely, with slight heating§. The radical nature of these reactions is confirmed not only by the clear signs of the polymerisation of tetrafluoroethylene[55] but also by the fact that a mixture of perfluoro-derivatives of bis(fluorosulphato)propane and bis(fluorosulphato)hexanes is formed from hexafluoropropene (in yields of 63 and 22% respectively)[151]:



Under very mild conditions (at −78 °C), peroxydisulphuryl difluoride adds to vinyl chloride and fluoride, but the compounds formed decompose on heating to room temperature[157].

The addition of peroxydisulphuryl difluoride to alkenes takes place non-stereospecifically. A mixture of *cis*- and *trans*-isomers is formed from 1,2-dichlorohexafluorocyclopentene[151], while acyclic internal C_4–C_6 *trans*-perfluoroolefins give rise to a mixture of *erythro*- and *threo*-isomers[193].

The exceptionally high reactivity of peroxydisulphuryl difluoride was manifested in its interaction with perfluorobenzene. It was found that the latter behaves in this instance as an unsaturated compound and readily combines with fluorosulphato-groups at 0–5 °C[195]:



One must note that the reaction is preferably carried out in an inert solvent, for example, in 1,1,2-trichlorotrifluoroethane, since in its absence there is an abrupt increase of temperature and pressure, which can lead to the ejection of the reaction mass[195]. At the beginning 1,4-addition of

§ The authors[151] note that, on heating a mixture of 1,2-dichlorohexafluorocyclopentene and peroxydisulphuryl difluoride from −30° to ~ 15 °C, a vigorous uncontrollable reaction is observed; satisfactory yields have been obtained only by adding the peroxide to the olefin heated to 50 °C.

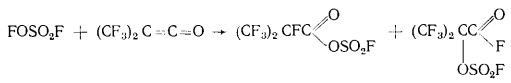
peroxydisulphuryl difluoride to perfluorobenzene takes place preferentially, but, even when an excess of perfluorobenzene by a factor of 1,5 together with 1,4-bis(fluorosulphato)perfluorocyclohexa-2,5-diene (I) is used, up to 10% of 1,2,3,4-tetrakis(fluorosulphato)perfluorocyclohex-5-ene (II) is formed. Possibly this can be explained by the fact that either the diene (I) is more reactive than hexafluorobenzene or by the partial 1,2-addition of peroxydisulphuryl difluoride, the conjugated diene being naturally more reactive. The hexene (II) as well as hexakis(fluorosulphato)perfluorohexane¶ can be obtained in quantitative yields using the corresponding molar amounts of the reactants, but the reaction with the third mole of peroxydisulphuryl difluoride is usually completed only after 5–6 h at 20–25 °C[195]:

$$3\,(OSO_2F)_2 + C_6F_6 \rightarrow C_6F_6(OSO_2F)_6 \ .$$

Halogen fluorosulphates add to alkenes still more vigorously than peroxydisulphuryl difluoride. The reagents diluted with nitrogen were initially combined *in vacuo* at room temperature. As a result, the corresponding fluorosulphonate esters were obtained from tetrafluoroethylene in a high yield[7]:

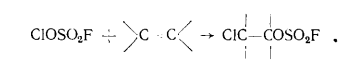
$$HalOSO_2F + CF_2{=}CF_2 \rightarrow HalCF_2CF_2OSO_2F \ ;$$
$$Hal{=}F,\ Cl,\ Br \ .$$

Fluorine fluorosulphate adds just as readily to tetrachloroethylene and perfluorocyclopentene[7], trichloroethylene (at −78 °C)[155], and a mixture of the *cis*- and *trans*-isomers of perfluorobut-2-ene[161]. A mixture of regioisomers has been obtained from bis(trifluoromethyl)keten in yields of 87 and 13%[194]:



However, β-fluoroethyl fluorosulphate could not be isolated from the products of the reaction of fluorine fluorosulphate and ethylene (*in vacuo* at −50 °C)[7].

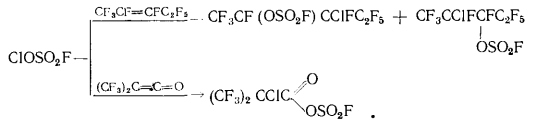
Apart from tetrafluoroethylene, fluoro- and chlorofluoroolefins are absorbed, as reported for the first time in 1973[196,197], by liquid chlorine fluorosulphate with a large exothermic effect at a temperature as low as 0–20 °C. On the basis of qualitative observations, the authors[196,197] reached the preliminary conclusion that the reactivity of the above olefins in the reaction with liquid chlorine fluorosulphate increases in the sequence which corresponds to their interaction with nucleophiles:



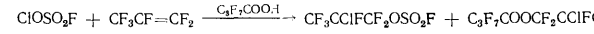
Continuation of research on these lines showed that chlorine fluorosulphate adds vigorously to trichloroethylene at temperatures between −50° and −55 °C[164], to tetrachloroethylene at −20 °C[78], and to trifluoroethylene, chlorotrifluoroethylene, perfluoropropene†, bis(trifluoromethyl)-keten[199], and *trans*-perfluorohex-2-ene[200] at temperatures as low as −65°–−70 °C, i.e. at the limit corresponding to the freezing of the mixture of reactants. However, it has been suggested[197] that the slow reaction of liquid chlorine fluorosulphate with tetrafluoroethylene is probably due to the poor solubility of the latter, since tetrafluoroethylene reacts with solutions of chlorine fluorosulphate in dichlorodifluoromethane or in 2-chlorotetrafluoroethyl fluorosulphate at a very high rate and a temperature as low as −70 °C[199]. Heating to 50–60 °C is required only for addition to 1,1-bis(fluorosulphonyl)difluoroethylene[201]:

$$ClOSO_2F + (FSO_2)C{=}CF_2 \rightarrow (FSO_2)_2\,CClCF_2OSO_2F \ .$$

Mixtures of regioisomers have been obtained in reactions with trifluoroethylene[199], chlorotrifluoroethylene[197,198], and *trans*-perfluoropent-2-ene[200], which can be explained in all probability by competition between the electronic and steric factors (the relative yields depend very little on the process temperature[199]). However, in contrast to the reaction with fluorine fluorosulphate[194], only one isomer is obtained from bis(trifluoromethyl)keten[199]:



In the presence of a perfluorocarboxylic acid, the interaction of chlorine fluorosulphate with perfluoropropene leads to a mixture of 2-chloroperfluoropropyl fluorosulphate and 2-chloroperfluoropropyl perfluorocarboxylate, the yield of the latter increasing with increasing excess of the acid[199]:



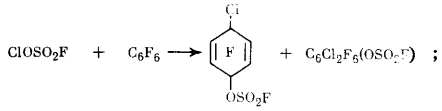
In the light of recent data[176,177], one cannot rule out the possibility that the formation of the ester is preceded by a stage involving the formation of the acyl hypochlorite.

At −100 °C chlorine fluorosulphate adds readily to ethylene[199] and at −30– −25 °C to acetylene, whose triple bond is fully saturated[164,189]:

$$ClOSO_2F + CH{\equiv}CH \rightarrow CHCl_2CH(OSO_2F)_2 + FSO_2OCHClCHClOSO_2F \ .$$

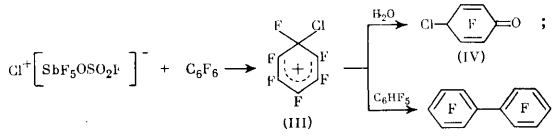
Symmetrical bis(fluorosulphato)dichloroethane was then obtained only in the form of an admixture (5–7%)[164].

Like peroxydisulphuryl difluoride but at an even lower temperature (between −20° and −25 °C), chlorine fluorosulphate reacts with perfluorobenzene[195]. The interaction with one mole also results in the formation of a 1,4-substituted cyclohexadiene containing an admixture (up to 10%) of a tetrasubstituted cyclohexene#. The latter as well as a hexasubstituted cyclohexane can be isolated in almost quantitative yields[195]:



$$3ClOSO_2F + C_6F_6 \longrightarrow C_6Cl_3F_6(OSO_2F)_3 \ .$$

The benzenium ion (III) can be generated by treating hexafluorobenzene with the complex of chlorine fluorosulphate and antimony pentafluoride, the hydrolysis of the ion yielding the ketone (IV) and its reaction with pentafluorobenzene giving rise to decafluorobiphenyl[191]:



¶ A mixture of stereoisomers is formed in both cases[195].

† The reaction has been carried out successfully also at −45 °C.[198]

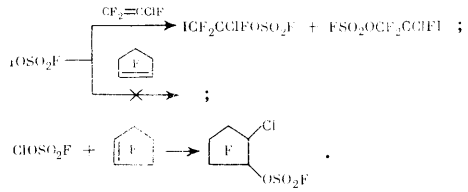
A complex mixture of regio- and stereo-isomers[195].

As already mentioned, bromine fluorosulphate adds exceptionally readily to tetrafluoroethylene[7] and also to hexafluoropropene[198] and perfluorobut-2-ene[160]. As in the case of chlorine fluorosulphate, the reaction with chlorotrifluoroethylene results in the formation of two regioisomers[160]. The product of the addition of bromine fluorosulphate to vinyl fluoride proved to be unstable[160].

The possibility of the addition of iodine fluorosulphate to alkenes was reported almost simultaneously by Fokin in Venice[189,202] and by Schack and Christe in San Francisco[203]. Iodine fluorosulphate is much less reactive in these reactions than fluorine, chlorine, or bromine fluorosulphates and interacts only slowly at 20–40 °C with tetrafluoroethylene, hexafluoropropene[202–204], partly fluorinated propenes, and vinylidene fluoride[205]. 2-Iodoperfluoroisobutyl fluorosulphate has been obtained in a yield less than 30% only after keeping the mixture of reactants at 20–25 °C for three weeks, but iodine fluorosulphate adds relatively easily to bis(trifluoromethyl)keten[205]:

$$IOSO_2F \left\{ \begin{array}{l} \xrightarrow{(CF_3)_2C=CF_2} (CF_3)_2CICF_2OSO_2F \ ; \\ \xrightarrow{(CF_3)_2C=C=O} (CF_3)_2CIC(O)OSO_2F \ . \end{array} \right.$$

Mixtures of regioisomers have been obtained from chlorotrifluoroethylene[203,205] and trifluoroethylene[205]. Iodine fluorosulphate does not add to perfluorocyclobutene[205] and perfluorocyclopentene[203], but chlorine fluorosulphate reacts readily with perfluorocyclopentene[203]:



2. Addition to Nitrogen–Carbon Multiple Bonds

Peroxydisulphuryl difluoride does not interact with perfluoro-2-azapropene[9] and perfluoro-2-azabut-1-ene[206]. The addition to pentafluoroguanidine is accompanied by the substitution of the difluoroamino-groups by fluorosulphato-groups[207,208], while the addition to fluorosulphonyl isocyanate under the influence of ultraviolet radiation is accompanied by the elimination of sulphur trioxide[209]:

$$(OSO_2F)_2 \left\{ \begin{array}{l} \xrightarrow{(F_2N)_2C=NF} (FSO_2O)_3CNFOSO_2F \ ; \\ \xrightarrow[FSO_2NCO,\,h\nu]{} FSO_2N(OSO_2F)C(=O)F + SO_3 \ . \end{array} \right.$$

Peroxydisulphuryl difluoride reacts under mild conditions with diazadienes—conjugated[77] and even those where the double bonds are separated by a sulphur atom[210]:

$$(OSO_2F)_2 \left\{ \begin{array}{l} \xrightarrow{(CF_3)_2C=NN=C(CF_3)_2} FSO_2OC(CF_3)_2N=NC(CF_3)_2OSO_2F \ ; \\ \xrightarrow{(CF_3)_2C=NSN=C(CF_3)_2} FSO_2OC(CF_3)_2N=S=NC(CF_3)_2OSO_2F \ . \end{array} \right.$$

The interaction of peroxydisulphuryl difluoride with chlorocyanogen and trifluoroacetonitrile at 80 °C is completed by the complete saturation of the triple bond, which the authors[211] explain by the intermediate formation of the nitrene (V), for example, via the mechanism

$$CF_3C\equiv N + \dot{O}SO_2F \rightarrow FSO_2OC(CF_3)=\dot{N} \ ;$$
$$FSO_2OC(CF_3)=\dot{N} + \dot{O}SO_2F \rightarrow \underset{(V)}{(FSO_2O)_2C(CF_3)\ddot{N}} \ ;$$
$$(FSO_2O)_2C(CF_3)\ddot{N} + (OSO_2F)_2 \rightarrow (FSO_2O)_2C(CF_3)N(OSO_2F)_2 \ .$$

In contrast to peroxydisulphuryl difluoride, chlorine and bromine fluorosulphates add exceptionally readily to perfluoro-2-azabut-1-ene[206] and pentafluoroguanidine[207,212]:

$$ClOSO_2F \left\{ \begin{array}{l} \xrightarrow{C_2F_5N=CF_2} C_2F_5NClCF_2OSO_2F \ ; \\ \xrightarrow{FN=C(NF_2)_2} FNClC(NF_2)_2OSO_2F \ . \end{array} \right.$$

Chlorine fluorosulphate interacts just as vigorously with trifluoromethyl, fluoroformyl, and trifluoroacetyl isocyanates[213], but fluorine fluorosulphate reacts with fluorosulphonyl isocyanate only under ultraviolet irradiation[209]:

$$ClOSO_2F + CF_3C(=O)NCO \rightarrow CF_3C(=O)NClC(=O)OSO_2F \ ;$$
$$FOSO_2F + FSO_2NCO \xrightarrow{h\nu} FSO_2N(OSO_2F)C(=O)F \ .$$

Despite the clear difference between the reaction mechanisms[209,213], the mode of addition indicated corresponds rigorously to the polarity of the reactants.

Only one mole of chlorine fluorosulphate adds easily to the nitriles of perfluorocarboxylic[168] and nitroperfluorocarboxylic[153] acids (at −40°–−30 °C) (in contrast to the reactions with peroxydisulphuryl difluoride[211]), for example:

$$ClOSO_2F + C_3F_7CN \rightarrow \underset{(VI)}{C_3F_7C(=NCl)OSO_2F} \ .$$

Treatment of the chloroimine (VI) with the second mole of chlorine fluorosulphate leads solely to the perfluoroacyl fluorosulphate and the anhydride of fluorosulphonic acid, approximately half of the chloroimine (VI) being converted. This can apparently be accounted for by the fact that the dichloroamine (VII) formed reacts with chlorine fluorosulphate more readily than the chloroimine (VI), splitting off the anhydride of fluorosulphonic acid and possibly nitrogen trichloride[168]:

$$C_3F_7C(=NCl)OSO_2F \xrightarrow{ClOSO_2F} \underset{(VII)}{[C_3F_7C(OSO_2F)_2NCl_2]} \xrightarrow{ClOSO_2F}$$
$$\rightarrow C_3F_7C(=O)OSO_2F + O(SO_2F)_2 + [NCl_3] \ .$$

Analogous results have been obtained also for the reactions of the nitriles of perfluorocarboxylic acids with two moles of chlorine fluorosulphate[168].

VI. OXIDATION OF CERTAIN NITROGEN-, SULPHUR-, SELENIUM-, AND IODINE-CONTAINING ORGANIC COMPOUNDS AS WELL AS CARBOXYLIC ACIDS

It is fairly difficult to achieve selective oxidation by the reagents considered, but in a series of instances this has been clearly demonstrated.

Peroxydisulphuryl difluoride oxidises almost quantitatively (yield 98%) bis(trifluoromethyl)hydroxylamine to bis(trifluoromethyl)nitroxide[77], from which only trifluoromethyl

fluorosulphate is formed subsequently, as from trifluoronitrosomethane[184]:

$$(OSO_2F)_2 + (CF_3)_2NOH \rightarrow (CF_3)_2NO \xrightarrow{(OSO_2F)_2} CF_3OSO_2F\ ,$$
$$(OSO_2F)_2 + CF_3NO \rightarrow CF_3OSO_2F\ .$$

Treatment of 2-nitrotetrafluoronitrosoethane with chlorine fluorosulphate leads to a chloroalkane and nitrosyl fluorosulphate[189]. An unstable, possibly salt-like, intermediate is apparently formed in the first stage and then decomposes under the usual conditions[189]:

$$R_FNO + ClOSO_2F \rightarrow R_FCl + NOSO_3F\ .$$

Trifluoromethanethiol is not oxidised unambiguously by peroxydisulphuryl difluoride, the product being a disulphide (yield 30%), from which trifluoromethyl fluorosulphate was subsequently obtained[77]. On the other hand, trifluorothioloacetic acid is converted qualitatively (for a molar reactant ratio of 2:1) into the corresponding disulphide, whose further treatment with peroxydisulphuryl difluoride yields trifluoroacetyl fluorosulphate[77]:

$$(OSO_2F)_2 \begin{cases} \xrightarrow{CF_3SH} (CF_3S)_2 + O(SO_2F)_2 + SO_2 + S\ ; \\ \xrightarrow{(CF_3S)_2} CF_3OSO_2F + SO_2 + S\ ; \\ \xrightarrow{2CF_3C(=O)SH} [CF_3C(O)S]_2 \xrightarrow{(OSO_2F)_2} CF_3C(O)OSO_2F + O(SO_2F)_2 + SO_2 + S\ . \end{cases}$$

The reaction of chlorine fluorosulphate with perfluoroalkyl and pentafluorophenyl diselenides is accompanied by the dissociation of the selenium–selenium bond[214]:

$$(CF_3Se)_2 + ClOSO_2F \rightarrow CF_3SeOSO_2F\ .$$

Only trifluoromethyl fluorosulphate was obtained initially from trifluoroiodomethane on treatment with peroxydisulphuryl difluoride[158] or chlorine fluorosulphate[165]:

$$ClOSO_2F + CF_3I \rightarrow CF_3OSO_2F\ .$$

However, in 1977 Naumann reported[215] that tervalent iodine compounds (VIII) are formed from perfluoroalkyl iodides and chlorine fluorosulphate in accordance with the mechanism

$$ClOSO_2F + R_FI \rightarrow [R_FICl OSO_2F] \xrightarrow{ClOSO_2F} \underset{(VIII)}{R_FI(OSO_2F)_2}\ .$$

Further study of this reaction showed that alkyl iodides are converted, on reaction with peroxydisulphuryl difluoride[204] or chlorine fluorosulphate[167] at a temperature as low as −50– −40 °C, into cream-coloured or white solid compounds of type (VIII), which decompose into alkyl fluorosulphates and iodine fluorosulphate when the alkyl radical has a straight-chain structure. Only perfluoroisopropyliodine bisfluorosulphate (m.p.101 °C) proved to be stable; on the basis of Raman spectra, the authors[167] attributed the dimeric structure (IX) to this substance:

$$RI \xrightarrow[[ClOSO_2F]]{(OSO_2F)_2} \underset{(VIII)}{RI(OSO_2F)_2} \xrightarrow{\sim 30-\ -20^\circ} ROSO_2F + IOSO_2F\ ;$$
$$R = CH_3,\ CF_3,\ C_3F_7,\ C_7F_{15}$$
$$(CF_3)_2CFI + ClOSO_2F \rightarrow \underset{(IX)}{\{[(CF_3)_2CF]_2I\}^+[I(SO_3F)_4]^-}\ .$$

Peroxydisulphuryl difluoride has been used successfully to synthesise iodine tristrifluoromethanesulphonate[216], but it was not possible to oxidise iodosyl trifluoromethanesulphonate to iodyl trifluoromethanesulphonate by this reagent as a consequence of the cleavage of the carbon–sulphur bond[112]:

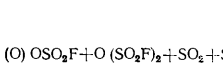
$$(OSO_2F)_2 \begin{cases} \xrightarrow{CF_3SO_3H,\ I_2} (CF_3SO_2O)_3I\ ; \\ \xrightarrow{CF_3SO_2OIO} CF_3OSO_2F\ . \end{cases}$$

It must be emphasised that apparently fairly extensive possibilities arise in processes of the type considered when peroxydisulphuryl difluoride is used *in situ*, i.e. in its electrochemical generation directly in the reaction mixture. Perfluoroalkyl fluorosulphates have been obtained by this method from perfluoroalkyl iodides in high yields and mono- and bis-fluorosulphates have been obtained from the di-iodo-derivatives[217], for example:

$$C_4F_9I \xrightarrow[HSO_3F/KSO_3F]{\text{electrolysis}} C_4F_9OSO_2F\ .$$

Carboxylic acids undergo mild oxidation to lactones (via fluorosulphato-substituted acids), from which cyclic unsaturated ketones are formed on keeping in the electrolyte for a longer period (up to 48 h)[218,219]. Unambiguous and readily reproducible results have been obtained for valeric and higher aliphatic acids as well as ω-cyclohexyl-substituted propionic and butyric acids. However, a mixture of 3- and 4-fluorosulphates (in proportions of 3:4) is obtained from the unsubstituted butyric acid, the yield of lactones being low and unstable. The sequence of transformations can be represented schematically as follows[219]:

$$RR'CH(CH_2)_nCOOH + HSO_3F \rightarrow FSO_3^- + RR'CH(CH_2)_nCO_2H_2^+ \rightarrow$$
$$\xrightarrow{(OSO_2F)_2} FSO_2OCRR'(CH_2)_nCO_2H_2^+ \rightarrow$$



R and R′ = H, alkyl, or cycloalkyl; n = 2 or 3.

The xenon difluoride–fluorosulphonic acid system, in which peroxydisulphuryl difluoride is formed[135–138] (see above), has been used to generate radical-cations from perfluoro-derivatives of naphthalene and biphenyl[139].

VII. CONCLUSION

The data described show that the reactions of peroxydisulphuryl difluoride and halogen fluorosulphates have been more widely investigated at present in relation to inorganic than organic compounds, this being confirmed also by the number of the corresponding publications. The very small number of kinetic studies, particularly on organic substances, is striking. Nevertheless the available information already provides an idea concerning the exceptionally high and extremely novel reactivity of the reagents considered and also about their extensive synthetic possibilities.

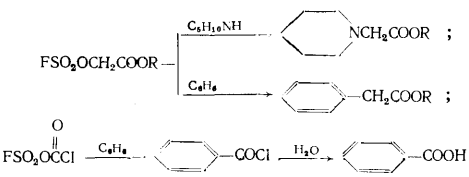
There is apparently no doubt about the radical nature of the absolute majority of the reactions of peroxydisulphuryl difluoride. The unusually high reactivity of the fluorosulphate radical is indicated, for example, by its ability to saturate perfluorobenzene completely at room temperature[195], whereas the analogous reaction of bis(trifluoromethyl)nitroxide requires prolonged heating at 120 °C.[220] Facts such as the necessity to add fluorosulphonic acid in order to substitute the chlorine atom in 1,1,2-trichlorotrifluoroethane[146] and also the substitution of the fluorosulphato-group in the ring and not the methyl group of toluene at temperatures below 0 °C are clear exceptions[77].

Except for fluorine fluorosulphate, which reacts via both radical and ionic mechanisms, halogen fluorosulphates are extremely vigorous electrophiles. Thus, despite the generally known inertness of perfluoro-olefins, particularly higher perfluoro-olefins, to the action of electrophiles, chlorine fluorosulphate adds readily to these compounds at temperatures as low as −65– −70 °C regardless of their structure[199] and at room temperature it adds to all the bonds of perfluorobenzene[195]. Chlorine fluorosulphate is apparently one of the strongest chlorinating agents, having a

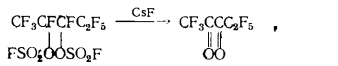
positively polarised chlorine atom, since, for example, its ability to chlorinate benzene to perchlorobenzene at −100 °C has no analogies in other systems[190].

The "anomalies" enumerated undoubtedly require further thought and study using modern methods of physicochemical analysis, possibly also as regards the reaction kinetics, in order to elucidate the true mechanisms of these phenomena.

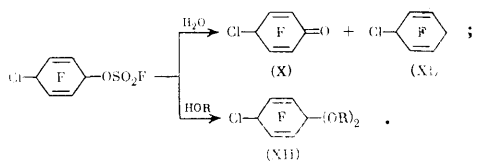
The possibility of introducing fluorosulphato-groups into various classes of organic compounds either by the addition of peroxydisulphuryl difluoride and halogen fluorosulphates to multiple carbon–carbon and carbon–nitrogen bonds§ or by the substitution of hydrogen, halogen, or certain functional groups. The fluorosulphato-group, which is one of the most readily eliminated groups, can be substituted in its turn by other functional groups on treatment with nucleophiles. The high reactivity of alkyl and acyl fluorosulphates is indicated, for example, by the alkylation of not only amines but also of benzene, even at reduced temperatures in the absence of a catalyst, by the relatively unstable fluorosulphatoacetate esters *in situ*[86,221] and also by the acylation of benzene by chlorocarbonyl fluorosulphate under approximately similar conditions[78]:



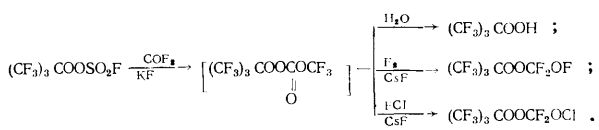
Primary perfluoroalkyl fluorosulphates are readily converted into the corresponding derivatives of perfluorocarboxylic acids, while the secondary compounds are converted into carbonyl compounds, for example into α-diketones[193]:



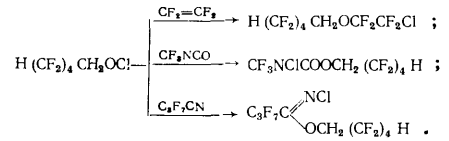
The diene (XI) is formed together with the ketone (X) from 4-chloroperfluoro-2,5-cyclohexadienyl fluorosulphate on hydrolysis, while treatment with alcohols leads to the stable ketals (XII)[222]:



Peroxy-compounds which could not be synthesised previously have been obtained from perfluoro-t-butylfluorosulphuryl peroxide[174,223]:



The hypochlorites derived from polyfluoro-alcohols, obtained by chlorination with chlorine fluorosulphate, also exhibit a high reactivity; they readily add to multiple carbon–carbon and carbon–nitrogen bonds[175,224]:



In conclusion we should like to emphasise that at present increasing attention is being devoted to the study of the properties and reactivities of the hypohalite derivatives of other strong acids such as nitric[10], perchloric[10,92–94], and trifluoromethanesulphonic[225,226]. Although many of these are much less stable than halogen fluorosulphates (for example, it has been recommended[226] that $ClOSO_2CF_3$ and $BrOSO_2CF_3$ are not heated above 0 °C), these compounds too are being used to an increasing extent in organic synthesis[10,225,226].

§ One cannot rule out the possibility that perfluoroazaalkenes do not react with peroxydisulphuryl difluoride[9,206] merely because of their poor solubility, as was observed previously in the reaction of tetrafluoroethylene with chlorine fluorosulphate[199].

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Fluorine-containing α-Dicarbonyl Compounds and Their Derivatives

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The synthesis of fluorine-containing α-dicarbonyl compounds and their derivatives, their chemical properties (including the formation of heterocycles), and their applications are considered. Data emphasising their characteristic features due to the presence of fluorine atoms are presented.
The bibliography includes 97 references.

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I. INTRODUCTION

α-Dicarbonyl compounds (α-DCC), namely α-diketones, α-ketoaldehydes, α-ketoacids, and their derivatives are used in industry and in laboratory syntheses. The presence of the α-dicarbonyl group in compounds of this class is responsible for their high reactivity in relation to many types of reagents. They are also convenient objects for the study of certain theoretical problems of organic chemistry (rotational isomerism relative to a single C–C bond and the mutual influence of substituents). Among compounds of this type, biologically active substances, analytical reagents, and valuable monomers have been discovered. The introduction of fluorine atoms into α-DCC molecules leads in many instances to a change of the reactivity of the substances and the appearance of new aspects of their applications. At the present time extensive data have accumulated in the literature on fluorine-containing α-DCC but no surveys on this problem have been published†.

This review surveys the literature data on the synthesis, chemical reactions, and practical applications of fluorine-containing α-diketones, α-ketoaldehydes, α-ketoacids, and their derivatives. The literature up to 1980 inclusive is covered.

II. METHODS OF SYNTHESIS

The preparation of a fairly large number of fluorine-containing α-diketones, α-ketoaldehydes, α-ketoacids, and their derivatives by various methods has been described in the literature; these data can be conveniently divided into two groups: the preparation of α-diketones and aldehydes and the preparation of α-ketoacids and their derivatives.

1. Fluorine-containing α-Diketones and α-Ketoaldehydes

A number of methods for the synthesis of fluorine-containing α-DCC are based on reactions of substances in which the carbonyl group is linked to a halogen atom and fluoroalkyl or fluoroacyl groups (acid halides, ketones, and acid anhydrides). These methods as a rule involve radical processes (the abstraction of radicals, recombination of fluoroacyl radicals, or oxidation).

† Some information about α-DCC is available in reviews[1,2] devoted mainly to other problems.

1,4-Difluorobutane-2,3-dione and 1,4-dichloro-1,4-difluorobutane-2,3-dione have been obtained (in yields of 42 and 58% respectively) by the reaction of monofluro- or chlorofluoro-acetyl chlorides with iron pentacarbonyl in an autoclave at 180 °C.[3] Diacetyl is formed by this method in 86% yield[3]:

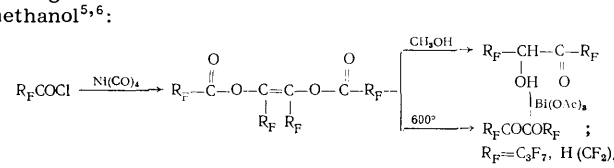
$$CHFXCOCl \xrightarrow[180°]{Fe(CO)_5} CHFXCOCOCHFX + CHFXCOF \ ; \quad X=H,Cl \ .$$

In the reactions of trifluoroacetyl and difluoroacetyl chlorides, perfluorodiacetyl and 1,1,4,4-tetrafluorobutane-2,3-dione are not formed, the degradation of the initial acid chlorides being observed with formation of iron fluorides, carbon, and small amounts of carbonyl fluoride and hexafluoroethane[3].

1,1,4,4-Tetrafluorobutane-2,3-dione and perfluorodiacetyl have been obtained by the reaction of difluoro- and trifluoroacetic anhydrides with iron pentacarbonyl (in yields of 11 and 6.5%).[4] Under the same conditions, diacetyl is formed from acetic anhydride in 90% yield[4]. Together with perfluorodiacetyl, the following compounds have been obtained from trifluoroacetic anhydride: iron trifluoroacetate, carbon monoxide, iron fluorides, trifluoroacetyl fluoride, hexafluorobut-2-en-2,3-diyl bistrifluoroacetate, and hexafluoroethane[4]. Analogous products are formed from difluoroacetic anhydride[4].

It is believed[3,4] that, with decrease of the fluorine content in the initial acid chlorides and anhydrides, the yield of acid fluorides falls, while that of α-diketones increases in connection with the decrease of the concentrations of iron fluorides in the reaction mixture.

When heptafluorobutyryl and ω-hydro-octafluorovaleryl chlorides react with nickel tetracarbonyl in benzonitrile at 25 °C, the corresponding enediol esters are formed in yields of 51 and 19%, the esters being converted into α-diketones by pyrolysis at 600 °C *in vacuo*[5,6]. The same α-diketones are formed on oxidation with bismuth triacetate of fluorine-containing α-ketonalcohols obtained from enediol esters and methanol[5,6]:



$$R_F = C_3F_7, \ H(CF_2)_4 \ .$$

The attempt to obtain decafluorobenzil from pentafluorobromo- or pentafluoroiodo-benzene and nickel tetracarbonyl in aprotic solvents was unsuccessful; the reaction products were only decafluorobiphenyl, decafluorobenzophenone, and pentafluorobenzene[7]. The authors[7] attribute the absence of

decafluorobenzil to the instability of the pentafluorobenzoyl radical, which decomposes before it can dimerise.

1,1,1-Trifluorobutane-2,3-dione and trifluoromethylglyoxyal are formed from ethyl trifluoromethyl ketone and trifluoroacetone when they are oxidised by selenium dioxide. However, these compounds could not be isolated in a pure state and they were characterised in the form of glyoximes[8]:

$$CF_3COCH_2X \xrightarrow{SeO_2} [CF_3COCOX] \xrightarrow{NH_2OH} \text{(dioxime)};$$

X=H, CH_3.

The above method is apparently without value for the synthesis of fluorine-containing α-DCC, because the attempt to hydrolyse perfluorodipropylglyoxime was unsuccessful[9]. More interesting results were obtained on oxidation of benzyl fluoroalkyl ketones[10]:

$$C_6H_5CH_2COC_3F_7 \xrightarrow{SeO_2} C_6H_5COCOC_3F_7;$$

$$C_6H_5CH_2CO(CF_2)_4COCH_2C_6H_5 \xrightarrow{SeO_2} C_6H_5COCO(CF_2)_4COCOC_6H_5.$$

In certain studies on the photolysis of hexafluoroacetone the formation of perfluorodiacetyl on recombination of trifluoroacyl radicals was postulated[11,12]. Although perfluorodiacetyl was not isolated in the above studies[11,12], in the investigation of the flash photolysis of hexafluoroacetone at −78 °C it was identified[12] from the phosphorescence spectra in the presence of hexafluoroacetone.

$$CF_3COCF_3 \xrightarrow{h\nu} CF_3COCOCF_3.$$

A large number of methods for the synthesis of fluorine-containing α-diketones, based on the reactions of compounds containing multiple bonds (fluoro-olefins, fluoroacetylenes, and fluoroallenes) have been described. Perfluorodiacetyl was synthesised for the first time by the oxidation of 2,3-dichlorohexafluorobut-2-ene with chromium trioxide in 20% oleum[13]. Trifluoroacetyl chloride and 2,3-dichloro-1,1,1,4,4,4-hexafluorobutylene sulphate are formed together with perfluorodiacetyl[13]:

$$CF_3CCl=CClCF_3 \xrightarrow[20\%\text{ oleum}]{CrO_3} CF_3COCOCF_3 + \text{(Cl, Cl, CF}_3\text{, O, O, S, O, O)} + CF_3COCl.$$

The above investigators studied the formation of perfluorodiacetyl in the oxidation of hexafluorobut-2-yne by chromium trioxide or potassium perchlorate in 20% oleum[14]:

$$CF_3CH=CHCF_3 \xrightarrow{27\%} CF_3COCOCF_3 \xrightarrow{7.3\%} CF_3CF=CFCF_3$$
$$CF_3C\equiv CCF_3 \xrightarrow{17\%} CF_3COCOCF_3 \xrightarrow{31-36\%} CF_3CCl=CClCF_3.$$

2,3-Dichlorohexafluorobutylene sulphate, formed on oxidation of 2,3-dichlorohexafluorobut-2-ene, is converted into perfluorodiacetyl on treatment with catalytic amounts of triphenylphosphine, triphenyl phosphite, tributylamine, or pyridine[15]:

$$\text{(Cl, Cl, CF}_3\text{, O, O, S, O, O)} \xrightarrow[80-90\%]{} CF_3COCOCF_3 + SO_2Cl_2.$$

Perfluorodiacetyl has been obtained from perfluorobut-2-ene via hexafluoro-2,3-dimethoxybutylene sulphate[16,17], formed in the reaction of sulphur trioxide with vicinal dimethoxy-derivatives of hexafluorobut-2-ene:

$$CF_3CF=CFCF_3 \xrightarrow{CH_3OH,\ CH_3ONa} CF_3C(OCH_3)=C(OCH_3)CF_3 \xrightarrow[-SO_2]{SO_3}$$
$$\rightarrow CF_3COCOCF_3 + \text{(OCH}_3\text{, OCH}_3\text{, CF}_3\text{, O, O, S, O, O)} \xrightarrow{H_2SO_4} CF_3COCOCF_3.$$
24% 79%

This is one of the best methods from the standpoint of the yields of products and the availability of the initial reactants. Unfortunately it is apparently not universal and is suitable only for the synthesis of perfluorodiacetyl, since, after the increase of the length of the fluoroalkyl residues, the reaction of the fluoro-olefin with sodium methoxide in methanol leads to the formation of mixtures of products[17].

Perfluorocyclobutane-1,2-dione has been synthesised in 30–50% yield on treatment of 1,2-dimethoxyperfluorocyclobutane with sulphuric acid[18]:

$$2CF_2=CFOCH_3 \longrightarrow \text{(OCH}_3\text{, F, F, OCH}_3\text{)} \xrightarrow{H_2SO_4} \text{(F, F, O, O)}.$$
83% 30–50%

Treatment of perfluorobut-2-ene with bromine fluorosulphate yielded 2,3-di(fluorosulphate)perfluorobutane, whose treatment with alkali metal fluorides did not permit the isolation of perfluorodiacetyl[19]. However, in another study[20] the reaction of bromine fluorosulphate with perfluorobut-2-ene yielded 2-bromo-3-fluorosulphatoperfluorobutane, which is converted into 2-bromoperfluoro-2-butanone on treatment with a caesium fluoride. The reaction of the butanone with peroxydisulphuryl difluoride yields 3-fluorosulphatoperfluoro-2-butanone, which reacts with caesium fluoride to form perfluorodiacetyl[20]:

$$CF_3CF=CFCF_3 \xrightarrow{BrOSO_2F} CF_3CF(OSO_2F)CFBrCF_3 \xrightarrow[-SO_2F_2]{CsF}$$
$$\rightarrow CF_3COCFBrCF_3 \xrightarrow[-BrOSO_2F]{(OSO_2F)_2} CF_3COCF(OSO_2F)CF_3 \xrightarrow[-SO_2F_2]{CsF} CF_3COCOCF_3;$$

$$CF_3CF\ CFCF_3 \xrightarrow{BrOSO_2F} CF_3CF(FO_2SO)CF(OSO_2F)CF_3 \xrightarrow{M} C_nF_{2n+2} + SO_2F_2 + CO_2 + CO + O_2.$$

The method of synthesis of symmetrical and asymmetric perfluoro-α-diketones by the reaction of peroxydisulphuryl difluoride with internal fluoro-olefins and subsequent treatment of the products with caesium fluoride is of undoubted interest[21].

Perfluoro-α-ketofluorosulphate-derivatives have now become fairly readily available as a result of their synthesis from the epoxy-derivatives of internal fluoro-olefins and fluorosulphonic acid, which made it possible to obtain a large number of fluorine-containing α-diketones[22–24].

$$R_FCF(O)CFR'_F \xrightarrow{HOSO_2F} R_FCF(OSO_2F)COR'_F + R_FCOCF(OSO_2F)R'_F \xrightarrow{CsF} R_FCOCOR'_F;$$
40–90%

R_F=CF_3, C_2F_5, C_3F_7; R'_F=CF_3, C_2F_5, C_3F_7, $CF(CF_3)_2$.

The last two methods are the most general for the synthesis of aliphatic and alicyclic perfluoro- α-diketones[21–24].

Perfluoro-2,5-dimethylhexane-3,4-dione has been isolated in 28% yield together with perfluoro-2,4-dimethyl-3-pentanone on reaction of perfluoropropene with oxalyl difluoride under pressure in acetonitrile in the presence of potassium hydrogen difluoride[25]:

$$CF_3CF=CF_2 + FOC-COF \xrightarrow[28\%]{KHF_2} (CF_3)_2CFCOCOCF(CF_3)_2 + (CF_3)_2CFCOCF(CF_3)_2.$$

An analogous but somewhat modified method, in which oxalyl dichloride can be used as the starting material, has also been proposed[26].

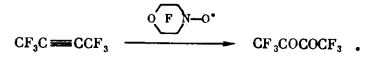
2-Chloroperfluoro-2-methylpentane-3,4-dione has been obtained with other products in 38% yield on treatment of tetrakis(trifluoromethyl)allene with nitrosyl chloride[27]:

$$(CF_3)_2C{=}C{=}C(CF_3)_2 \xrightarrow[180°]{NOCl} \underset{38\%}{CF_3COCOCCl(CF_3)_2} .$$

When hexafluorobut-2-yne or perfluorodiphenylacetylene reacts with bis(trifluoromethyl)nitroxide, perfluorodiacetyl or decafluorobenzil are formed in yields of 73% (for a 50% conversion) and 25% respectively[28]:

$$R_FC{\equiv}CR_F \xrightarrow{(CF_3)_2NO^\bullet} R_FCOCOR_F ;$$
$$R_F{=}CF_3,\ C_6F_5 .$$

Hexafluorobut-2-yne also gives rise to perfluorodiacetyl on reaction with perfluoromorpholine oxide[29]:



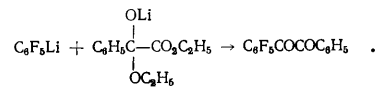
α-Diketones containing pentafluorophenyl groups are synthesised mainly with the aid of aromatic organometallic compounds. Decafluorobenzil is formed in 43–55% yield when pentafluorophenyl-lithium reacts with dimethyl oxalate at low temperatures (between −40° and −78 °C): [30]

$$C_6F_5Li + CH_3OOC-COOCH_3 \rightarrow C_6F_5COCOC_6F_5 .$$

Decafluorobenzil can be obtained in 26–32% yield from phenylcopper and oxalyl dichloride in ether[31]:

$$C_6F_5Li + CuBr \rightarrow C_6F_5Cu \xrightarrow{ClOC-COCl} C_6F_5COCOC_6F_5 .$$

Pentafluorobenzil can be obtained in 40% yield via the following mechanism[30]:



Pentachloropentafluorobenzil has been synthesised by the reaction of pentafluorophenyl-lithium with methyl pentachlorobenzoyl formate at −78 °C (yield 87%): [30]

$$C_6F_5Li + C_6Cl_5COCO_2CH_3 \rightarrow C_6F_5COCOC_6Cl_5 .$$

2. Fluorine-Containing α-Ketoacids and Their Derivatives

The main methods of synthesis of fluorine-containing α-ketoacids and their derivatives involve the interaction of the epoxy-derivatives of terminal fluoro-olefins and perfluoroazirines with nucleophiles (H_2O, ROH, RNH_2) or electrophiles (SO_2).

The hydrate of trifluoropyruvic acid has been obtained by treating epoxyhexafluoropropane with water[32,33]. This method proved to be general and has been used successfully to synthesise the hydrates of fluorine-containing α-ketoacids with longer fluoroalkyl residues from the corresponding epoxy-derivatives of higher fluoro-olefins[34,35]:

$$R_FCF{-}CF_2 \xrightarrow{H_2O} \underset{40-80\%}{R_FCOCO_2H{\cdot}H_2O} ,$$

$R_F{=}CF_3$ [32, 33]; C_2F_5 [34]; $H(CF_2)_n$, where n = 2, 4 [34], 6 [35]; C_4F_9 [34].

The synthesis of trifluoropyruvic acid by the hydrolysis of perfluoro-2-methyl-2*H*-azirine and perfluoro-3-methyl-2*H*-azirine has been described[36]:

$$CF_3CF{-}CF \xrightarrow[70°]{H_2O} [CF_3COCO_2H] \xrightarrow{C_6H_5NH_2} \underset{33\%}{CF_3COCO_2^-\overset{+}{N}H_3C_6H_5} .$$

The hydrate of trifluoropyruvic acid is formed on acid hydrolysis of α,α-diaminoperfluoropropionamide[37]:

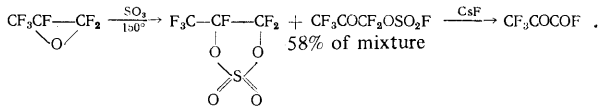
$$CF_3CF{-}CF_2 + H_2NR \rightarrow CF_3C(NHR)_2CONHR \xrightarrow{H_2O,\ H_3PO_4} CF_3COCO_2H{\cdot}H_2O .$$

On the interaction with water, the fluoride of trifluoropyruvic acid yield trifluoropyruvic acid hydrate; the starting materials for the synthesis of the acid fluoride are epoxyhexafluoropropane and an aromatic carbonyl compound (benzophenone, acetophenone, benzaldehyde, etc.)[38–45]:

$$CF_3CF{-}CF_2 \xrightarrow{ArCOR} CF_3COCOF + CF_3COF$$
$$\downarrow H_2O$$
$$CF_3COCO_2H{\cdot}H_2O \xrightarrow{H_2SO_4} CF_3COCO_2H .$$

One must note that the mechanism of this reaction still remains obscure.

The fluoride of trifluoropyruvic acid has also been obtained from epoxyhexafluoropropane and sulphur trioxide at 150 °C with subsequent elimination of sulphuryl fluoride by treating the mixture of the addition products with caesium fluoride[46]:

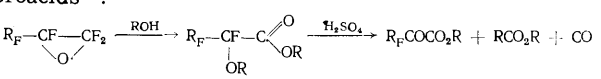


Pyrolysis of 1-nitro-perfluoro-2-propyl nitrite in a flow system gives rise to trifluoropyruvyl fluoride in a yield of approximately 10%: [47]

$$O_2N{-}CF_2{-}\underset{\underset{ONO}{|}}{CF}{-}CF_3 \xrightarrow{250°} CF_3COCOF + NO .$$

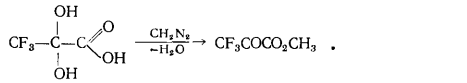
The study of the infrared spectra and of the temperature variation of the ^1H NMR spectra of solutions of hydrated fluorine-containing α-ketoacids showed that they exist in the form of fluoro-α,α-dihydroxyacids $R_FC(OH)_2COOH$. They differ in this respect from the usual fluorine-free α-ketoacids, which do not form stable hydrates capable of being isolated in a crystalline form[34].

On treatment of the hydrates of fluorine-containing α-ketoacids with phosphorus pentoxide, the anhydrous α-ketoacids are formed[35]. The alkyl esters of carboxylic 2-alkoxyperfluoroacids have been synthesised in high yields (50–96%) by the reaction of the epoxy-derivatives of terminal fluoro-olefins with alcohols[32,33,48–51]. Methyl tetrafluoro-2-methoxypropionate is converted on treatment with sulphuric acid at 140 °C into methyl trifluoropyruvate[48]. However, the alkyl esters of higher carboxylic 2-alkoxyfluoroacids give rise under these conditions to a mixture of alkyl esters of carboxylic fluoro-α-ketoacids and the products of the decarbonylation of the esters of the corresponding carboxylic fluoroacids[51]:

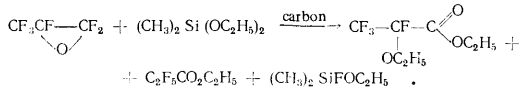


R = alkyl, $R_F = CF_3$ (Ref.48; C_2F_5 (Ref.51); C_4F_9(Ref.51); $H(CF_2)_n$, where n = 2, 4 (Ref.51).

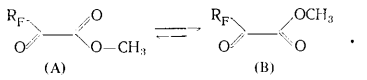
By reducing the reaction temperature to 100 °C or 60 °C (on replacing sulphuric acid with 20% oleum), it was possible to obtain the pure methyl esters of higher polyfluoro-α-ketoacids[51]. Methyl trifluoropyruvate has been obtained by treating the hydrate of trifluoropyruvic acid with diazomethane[48]:



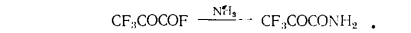
Ethyl 2-ethoxytetrafluoropropionate is formed when epoxyhexafluoropropane reacts with diethoxydimethylsilane[52]:



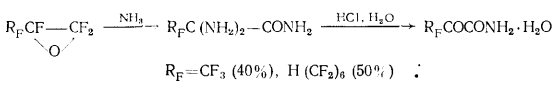
The study of the infrared spectra and dipole moments of solutions of the methyl esters of fluorine-containing α-ketoacids in carbon tetrachloride established that they exist in the form of equilibrium mixtures of the *trans*- and *cis*-conformers (A) and (B) with the *cis*-form predominating[53]. Pyruvate esters also consist of mixtures of the *cis*- and *trans*-conformers but with the *trans*-form predominating[54]. This difference is apparently due to the fact that the *cis*-forms of the esters of fluorine-containing α-ketoacids are less polar than the *trans*-forms, whereas in the case of the esters of hydrocarbon α-ketoacids the *trans*-form is less polar:



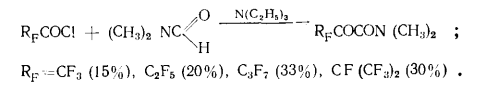
The amide of trifluoropyruvic acid has been obtained by the reaction of the corresponding acid fluoride with ammonia[38,40,43]:



Hydrolysis of the amides of carboxylic α,α-diaminofluoroacids leads to the hydrates of the amides of α-ketoacids[35]:



The synthesis of the dimethylamides of carboxylic fluoro-α-ketoacids by the reaction of the chlorides of carboxylic perfluoroacids with dimethylformamide in the presence of triethylamine has been described[55,56] (without triethylamine, the yields are much lower[55,56]):



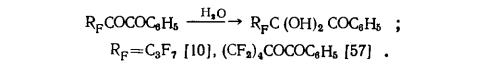
III. CHEMICAL REACTIONS

1. Anionoid Reactions

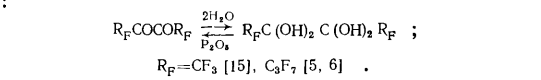
The majority of the studies in the chemistry of the fluorine-containing α-DCC have been associated with the investigation of anionoid reactions; they lead to different valuable α-DCC derivatives and make it possible to synthesise compounds with practically useful properties.

(a) The Interaction of α-DCC with Hydroxy-compounds

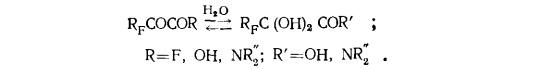
Fluorine-containing α-diketones with a fluoroalkyl substituent at one of the carbonyl groups and bis- α-diketones with an aliphatic fluorine-containing chain between the α-dicarbonyl groups combine with one molecule of water to form *gem*-ketodiols[10,57]. The site of addition has not been rigorously demonstrated but, by analogy with asymmetric β-diketones for which the addition of water to the carbonyl group linked to the fluorine-containing substituent has been established by ^1H, ^{19}F, and ^{13}C NMR, one can assume that in the case of the α-diketones water also reacts with the carbonyl group adjoining the fluorinated substituent[58]:



α-Diketones in which the fluoroalkyl groups are linked to both carbonyl groups combine with two water molecules to form tetraols[5,15]. The tetraols are stable compounds and give up water only on heating with phosphorus pentoxide[5,6] or 20% oleum[15]:

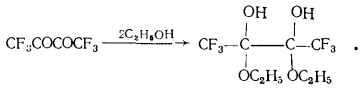


Fluorine-containing α-ketoacids[32,33,35,37], acid fluorides[37,38], and amides[35,55] also combine with a water molecule at the carbonyl group to form *gem*-dihydroxy-derivatives. The acid fluoride group is then hydrolysed to the carboxy-group:

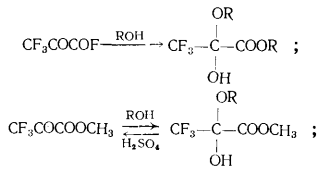


The derivatives of α,α-dihydroxy-acids are entirely stable compounds which give up water only on treatment with phosphorus pentoxide[47] or sulphuric acid[38], while the hydrocarbon α-ketoacids do not form stable hydrates.

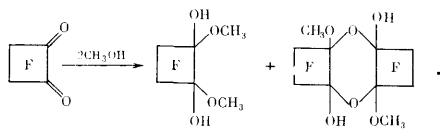
On interaction with ethanol, perfluorodiacetyl gives rise to a stable bishemiketal[14]:



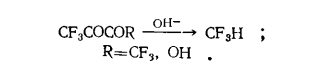
The methyl ester[37,60] and fluoride[61] of trifluoropyruvic acid react vigorously with alcohols, which leads to stable hemiketals. The hemiketal of methyl trifluoropyruvate can be decomposed by treatment with sulphuric acid[60]:



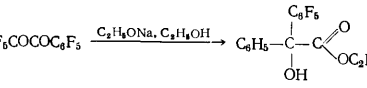
Perfluorocyclobutane-1,2-dione gives rise to a mixture of a bishemiketal and a dioxan on treatment with methanol[18]:



When aliphatic fluoro-α-diketones[14] and fluoro-α-ketoacids[33] are treated with aqueous alkali, they undergo the haloform decomposition with formation of trifluoromethane, like the fluorinated monoketones[59]:

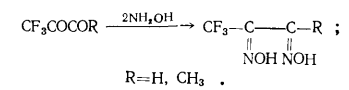


Fluorine-containing aromatic α-diketones in alcohol undergo a rearrangement in the presence of alkali metal alkoxides with migration of the pentafluorophenyl group[30]:



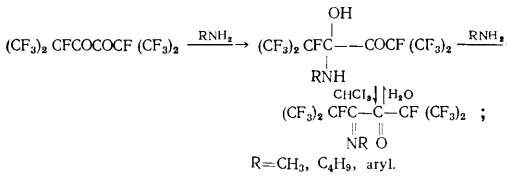
(b) The Interaction of α-DCC with Amino-Nucleophiles

The interaction of α-dicarbonyl compounds having one fluoroalkyl group with hydroxylamine yields dioximes, which readily form complexes with the nickel cation[8]:



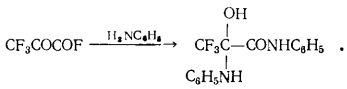
R=H, CH_3 .

Perfluoro-2,5-dimethylhexane-3,4-dione reacts with amines (with the reactants in proportions of 1:1) to form adducts which split off water on heating in chloroform and yield ketoimines[26]. However, on treatment with an excess of the amine, the α-diketone or its 1:1 adduct with the amine undergo the haloform decomposition with formation of 2-hydroperfluoropropane[26], which is apparently associated with the great stability of the leaving heptafluoroisopropyl anion:

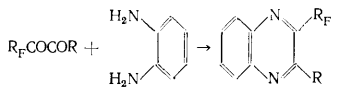


R=CH_3, C_4H_9, aryl.

When trifluoropyruvyl fluoride was allowed to react with aniline the anilide of α-hydroxy-α-phenylaminoperfluoropropionic acid was obtained[46]:

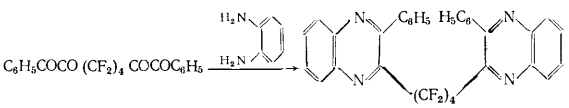


Fluorine-free α-diketones react with *o*-phenylenediamine (OPDA) to form 2,3-substituted quinoxalines[62]. This reaction has been studied vigorously also in the series of fluorine-containing α-DCC. Investigations showed that fluorine-containing α-diketones with fluoroalkyl substituents having a straight-chain structure and aromatic fluoro-substituents react with OPDA like the α-diketones of the hydrocarbon series and give rise to satisfactory yields of quinoxalines containing fluorinated substituents in the heterocyclic ring[5,8,10,14,30]. The reaction has been used successfully to identify fluorine-containing α-diketones, since the quinoxalines formed are readily purifiable crystalline substances.

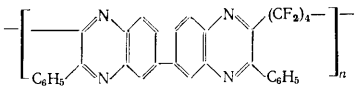


R_F=CF_3, R=H [8]; R_F=CF_3; R=CH_3 [8]; R_F=R=CF_3 [14]; R_F=C_3F_7, R=C_6H_5 [10]; R_F=R=C_3F_7 [5]; R_F=R=H$(CF_2)_4$ [5]; R_F=R=C_6F_5 [30] .

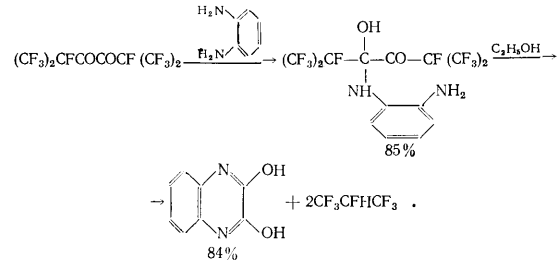
Fluorine-containing bis-α-diketones with an aliphatic fluorinated chain between the α-dicarbonyl groups also react with OPDA and give rise to bis-quinoxalines[57]:



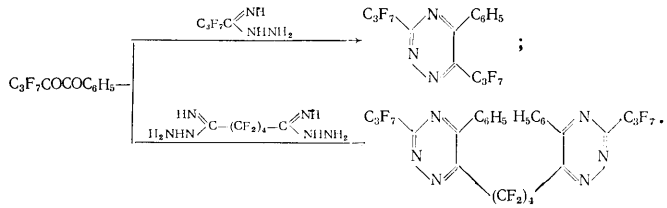
This synthesis has been used to obtain polyquinoxalines by the reaction of bis-α-diketones with tetra-aminobiphenyl[57]:



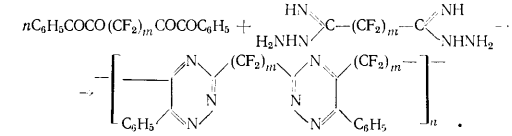
Perfluoro-2,5-dimethylhexane-3,4-dione reacts with OPDA in an unusual manner. Thus in acetonitrile at 0 °C the product is a 1:1 adduct, formed in 85% yield, which on heating in alcohol eliminates 2-hydroheptafluoropropane with formation of 2,3-dihydroxyquinoxaline[26,63]. This reaction pathway agrees also with the reactivity in relation to primary amines[26]; it too can be explained by the high stability of the leaving perfluoroisopropyl anion:



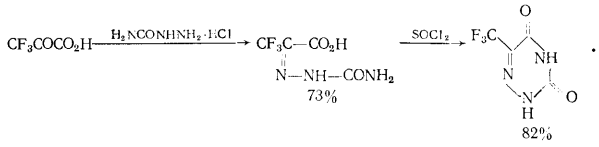
The interaction of fluorine-containing α-diketones with the imidoylhydrazides of carboxylic perfluoroacids, which leads to asymmetric triazines and bistriazines, has been described[10]:



If a bis-α-diketone and the bisimidoylhydrazide of a dicarboxylic perfluoroacid are introduced into the reaction, then fluorine-containing asymmetric polytriazines are formed[57]:



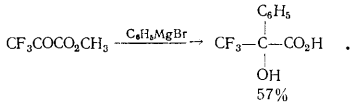
The interaction of trifluoropyruvic acid with semicarbazide hydrochloride in water yielded the semicarbazone of trifluoropyruvic acid, which is converted into 5-trifluoromethyl-6-azauracil on being refluxed with thionyl chloride[64]. The uracil has been used to synthesise nucleosides and nucleotides[64]:



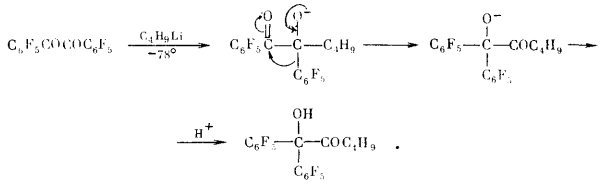
It follows from the available literature data on the interaction of α-DCC with hydroxy- and amino-nucleophiles that the introduction of fluorine into the α-DCC molecule reduces the electron density at the carbonyl carbon atoms, as a result of which they are capable of forming stable adducts via one or both carbonyl groups, which is not characteristic of fluorine-free α-DCC. The structure of the fluorinated substituent also has a considerable influence on the reactivity of the α-DCC. Thus the introduction of perfluoroisopropyl groups gives rise to an increased tendency of perfluoro-2,5-dimethylhexane-3,4-dione to undergo the haloform decomposition in the presence of bases[36,63].

(c) The Interaction of α-DCC with Organometallic Compounds

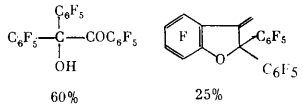
Treatment of methyl trifluoropyruvate with phenylmagnesium bromide and subsequent treatment of the reaction mixture with sulphuric acid and an alkali yielded α-hydroxy-α-trifluoromethyl phenylacetic acid[65]:



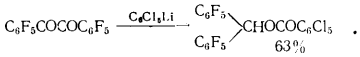
The reactions of alkyl- and aryl-lithium compounds with fluorine-containing aromatic α-diketones result in the formation of adducts, which undergo a rapid rearrangement with migration of the pentafluorophenyl group[30]. The structure of the final reaction products depends on the nature of the lithium derivative used. Thus, when decafluorobenzil was treated with butyl-lithium, 2-hydroxy-1,1-bis(pentafluorophenyl)-2-hexanone was obtained after acid hydrolysis[30]:



The interaction of decafluorobenzil with pentafluorophenyllithium leads to the formation of perfluoro-2-benzylbenzoin and perfluoro-2,2-diphenylbenzofuran-3-one (the latter is obtained as a result of the intramolecular nucleophilic substitution of the *ortho*-fluorine atom)[30]:



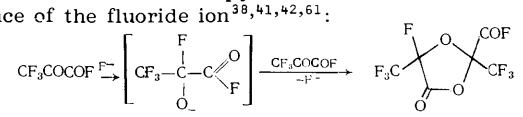
The reaction with pentachlorophenyl-lithium results in the formation of bispentafluorophenylmethyl pentachlorobenzoate[30]:



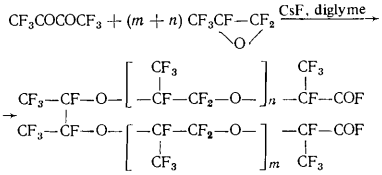
(d) Reactions with Participation of the Fluoride Anion

The reactions with participation of the fluoride anion are important for the chemistry of fluorinated carbonyl compounds[66,67]. However, hitherto only a limited number of reactions involving the fluoride ion in the series of fluorine-containing α-DCC are known.

The fluoride of trifluoropyruvic acid dimerises in the presence of the fluoride ion[38,41,42,61]:

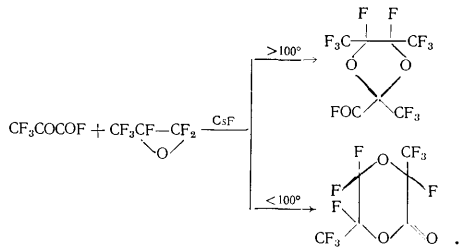


In the presence of caesium fluoride, perfluorodiacetyl reacts with epoxyhexafluoropropane in diglyme to form oligomeric products, both carbonyl groups of perfluorodiacetyl being involved in the reaction[69]:



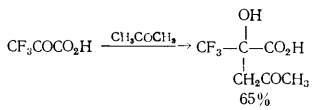
The acid fluoride groups of this oligomer were then converted into fluoroalkyl groups by reaction with elemental fluorine[69].

The interaction of epoxyhexafluoropropane with the fluoride of trifluoropyruvic acid and caesium fluoride leads to dioxolan or dioxan derivatives, depending on the temperature[38,40,43,44]:

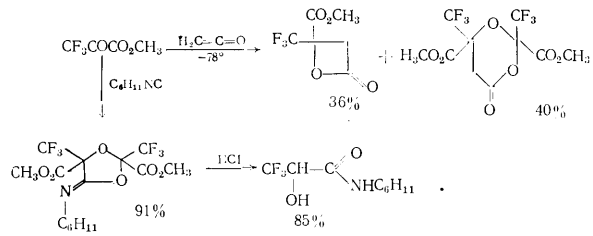


(e) Other Reactions of α-DCC with Participation of the Carbonyl Group

The condensation of trifluoropyruvic acid with acetone in water has been observed. The reaction in the formation of α-hydroxy-α-trifluoromethyl-γ-oxovaleric acid[32]:



When methyl trifluoropyruvate was allowed to react with keten, β-methoxycarbonyl-β-trifluoromethyl-β-propiolactone and 2,4-bis(methoxycarbonyl)-2,4-bis(trifluoromethyl)-1,3-dioxan-6-one were obtained[60]. Treatment of methyl trifluoropyruvate with cyclohexyl isocyanide in the same study[60] led to the isolation of a high yield of 5-cyclohexylimino-2,4-bis(methoxycarbonyl)-2,4-bis(trifluoromethyl)dioxolan, whose acid hydrolysis results in the formation of the cyclohexylamide of trifluorolactic acid:

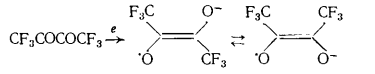


2. Oxidation-Reduction Reactions

The fluorine-free α-DCC are capable of undergoing oxidation-reduction reactions with participation of the carbonyl groups[70]. The oxidation-reduction reactions of polyfluoro-α-DCC with participation of the carbonyl groups (electrochemical reduction[71,72], interaction with metals and their salts[71,75], and interaction with phosphorus-containing reagents[77–86]) are also known.

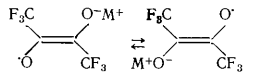
(a) Reduction of α-DCC

Like diacetyl, hexafluorodiacetyl is converted on electrochemical reduction in tetrahydrofuran (THF) (in the presence of an R_4N^+ cation) into a semidione radical-anion, which exists in the form of an equilibrium mixture of the *trans*- and *cis*-isomers (as shown with the aid of EPR).[71,72] The *trans/cis* ratio is 170 in THF and 120 in dimethyl sulphoxide (DMSO):[71,72]

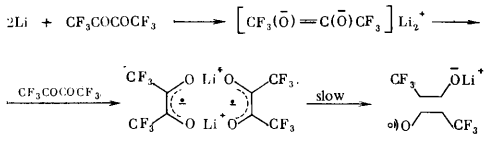


The *trans/cis* ratio for diacetyl in DMSO (in the presence of an R_4N^+ cation) is 35;[70] thus the introduction of fluorine shifts the equilibrium towards the *trans*-isomer.

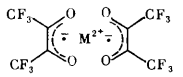
On interaction with alkali and alkaline earth metals in DMSO and THF, hexafluorodiacetyl is reduced to a radical-anion[71], which gives rise to several types of ion pairs with metal cations. If the counterions are Cs^+ and Rb^+, then the *trans*-isomer is formed preferentially (*trans/cis* = 150, DMSO, Rb^+; *trans/cis* > 200, THF, Cs^+);



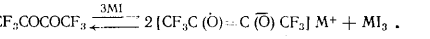
The mechanism of the interaction of hexafluorodiacetyl with lithium has been established by EPR[71]:



The formation of ion pairs on reduction of perfluorodiacetyl with alkaline earth metals (Ca, Sr, and Ba) in THF was demonstrated in the same study[71]:

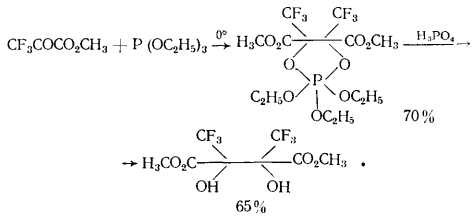


Hexafluorodiacetyl is also reduced on treatment with alkali metal iodides in solvents [in DMSO, hexamethylphosphoramide (HMP), and ethereal solvents] to a radical-anion, which forms ion pairs with alkali metal cations[72,74]. In DMSO and HMP the radical-anion exists mainly in the *trans*-form, (*trans/cis* > 100) and the ratio of the isomers is independent of the nature and the concentration of the counterion. The reduction takes place rapidly also in ethereal solvents when lithium iodide is used as the reductant[72], 1 : 1 ion pairs being formed. In the reaction involving treatment with sodium iodide, irradiation with light from a mercury lamp in a quartz cell is required[72]:



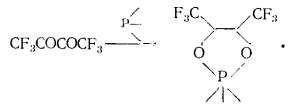
(b) The Interaction of α-DCC with Fluorine-Containing Reagents

The product of the reaction of methyl trifluoropyruvate with triethyl phosphite is a 2 : 1 adduct consisting of a cyclic phosphorane whose hydrolysis gives rise to a pinacone[60]:

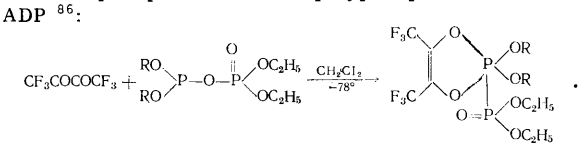


It is of interest that trifluoropyruvate reacts via one carbonyl group, like hexafluoroacetone, and not a diketone in which both carbonyl groups are reduced with formation of 1,3,2-dioxaphospholens[76].

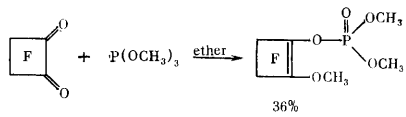
Numerous studies have been devoted to the investigation of the reactions of hexafluorodiacetyl with phosphorus(III) derivatives of different structure. A series of cyclic 1,3,2-dioxaphospholens have been obtained in this way with high yields[77–86]:



For example, hydroxyphosphoranes have been synthesised in this way from hexafluorodiacetyl and mixed anhydrides of phosphoric and phosphorous acids, which are models of the hypothetical intermediates formed in the addition of nucleophiles to the phosphorus atom in polyphosphates such as ATP and ADP [86]:

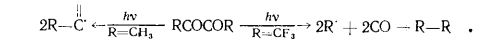


In reactions with phosphorus(III) derivatives, fluorine-containing aliphatic α-diketones behave mainly analogously to fluorine-free α-diketones[87]. It is of interest that the reaction of perfluorocyclobutane-1,2-dione with trimethyl phosphite yields dimethyl 3,3,4,4-tetrafluoro-2-methoxycyclobut-1-enyl phosphate[88].

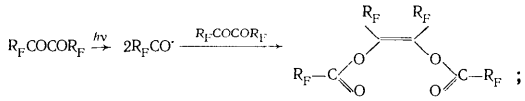


3. Radical Reactions

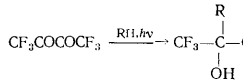
When hexafluorodiacetyl is irradiated with ultraviolet light in the vapour phase, it decomposes into trifluoromethyl radicals and carbon monoxide[89,90]. Irradiation of diacetyl at room temperature leads to the formation in the primary photochemical step of two acyl radicals, which then undergo a number of reactions[91]:



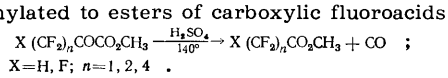
The study of the photolysis of hexafluorodiacetyl and tetrafluorodiacetyl in the liquid phase showed that the trifluoroacetyl radicals arising in the first stage can interact with the initial diketones to form diacetyl derivatives of enediols[4]:



When hexafluorodiacetyl is exposed to ultraviolet light in the presence of hydrocarbons, ketoalcohols and small amounts of CO are formed[90]:



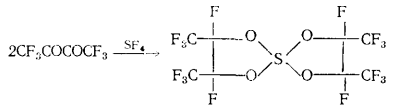
When the methyl esters of polyfluoro-α-ketoacids are heated above 140 °C in the presence of sulphuric acid, they are decarbonylated to esters of carboxylic fluoroacids[51]:



One must note that the available literature data are insufficient to reach conclusions concerning the pathways followed in the primary photochemical processes in the photolysis of fluorine-containing α-DCC.

4. Interaction with Sulphur Tetrafluoride

The unusual formation of a spirosulphuran (in a quantitative yield) on interaction of hexafluorodiacetyl with sulphur tetrafluoride (reactant ratio 2:1) has been observed[92]. The compound obtained is a stable crystalline substance whose structure has been determined by ^{19}F and ^{13}C NMR and by X-ray diffraction[92]. It is of interest that products of the fluorination of the carbonyl groups of hexafluorodiacetyl were not detected in the reaction mass, whereas in the series of hydrocarbon α-DCC such compounds are formed in high yields[92-96]:



IV. APPLICATIONS

Perfluorodiacetyl has been recommended as an antibacterial and fungicidal agent and also for imparting water- and dirt-repellent properties to cotton textiles[13]. The use of perfluorodiacetyl as a photoinitiator in radical polymerisation and also for the treatment of fabrics has been patented[16].

The fluoride of trifluoropyruvic acid and its cyclic dimer are used as soil fumigants and insecticides, which evolve hydrogen fluoride on contact with water[39,41].

The amide of trifluoropyruvic acid can be used as a dispersing agent and exhibits surface-active properties[41].

The fluoride of trifluoropyruvic acid serves as the starting material for the synthesis of perfluoro-derivatives of cyclic dioxans and dioxolans, which are chemically inert and thermally stable solvents[41]. This compound is used as the starting material for the synthesis of monomers and then polymers employed as adhesive films and films with irreversible gas permeability[45]. The latter can be used to separate different gases.

Glyoximes, which are used as reagents for nickel(II), have been obtained from 1,1,1-trifluorobutane-2,3-dione and trifluoromethylglyoxal[8].

Polymers with quinoxaline and triazine rings in the chain have been obtained from fluorine-containing bis-α-diketones having an aliphatic fluorine-containing chain between the α-dicarbonyl groups[57]. Fluorine-substituted benzils are used as the starting materials for the synthesis of anaesthetics and antihistamine preparations[97].

Analysis of the present state of research into the chemistry, properties, and applications of fluorine-containing α-dicarbonyl compounds (α-diketones, α-ketoaldehydes, α-ketoacids, and their derivatives) permits the conclusion that methods have been developed in recent years for their synthesis and their properties of practical value have been discovered. However, hitherto many problems of the chemistry of α-dicarbonyl compounds have been virtually uninvestigated. Thus there are almost no data on their reactions with electrophiles and few studies have been made on the radical processes and physicochemical properties of substances in this series; such studies would yield additional information about the influence of fluorine atoms on the reactivity of organic compounds.

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The Reactivity of 1,3,2-Diheterophospholans and 1,3,2-Diheterophosphorinanes with a Tetracoordinate Phosphorus Atom

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The present state of research into the reactivities of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes with a tetracoordinate phosphorus atom, containing in five- and six-membered rings, two identical or two different hetero-atoms (O, S, or N) together with the phosphorus atom, is described. Attention is concentrated on the differences between the reactivities of cyclic and acyclic organophosphorus compounds with the same ligand environment of the phosphorus atom. The influence of the introduction of a phosphorus atom into the ring on the reactivity of cyclic compounds is demonstrated. The bibliography includes 189 references.

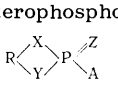
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I. INTRODUCTION

The last decade has been marked by increasing interest in cyclic esters, thioesters, amides, and amidoesters of phosphorus acids in which a tetracoordinate phosphorus atom is incorporated in a five- or six-membered ring—1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes. The importance of studies on organophosphorus compounds of this type is due primarily to the important role of cyclic phosphates in many biochemical processes. The considerable distortion of the geometry of the phosphorus tetrahedron in cyclic structures, particularly in five-membered structures, and the resulting changes in the nature of the intramolecular electronic interactions predetermine the known specificity of the reactivity of such molecules, differing significantly in many instances from the reactivity of their acyclic analogues. In addition, the rigidity of the cyclic fragment is responsible for certain limitations in the relative positions of the ligands at the phosphorus atom, imposing thereby its imprint on the stereochemical results of processes involving such molecules.

The aim of the present review is to examine and as far as possible describe systematically and survey the results of studies on the reactivities of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes having the general formula



R = 1,2- and 1,3-alkylene or 1,2- or 1,3-arylene; X, Y = O, S, NR'; Z = O, S, Se, NR'; A = = Alk; Ar, AlkO; ArO, AlkS, ArS, NR'_2, OH, SH, H .

Particular attention has been devoted to the deduction of the chemical consequences of the incorporation of a tetracoordinate phosphorus atom in the cyclic skeleton of the molecule; the reactivities of cyclic and acyclic compounds with the same ligand environment of the phosphorus atom have been compared.

Mainly synthetic aspects of the chemistry of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes have been considered in the available review literature[1]. Much attention has been devoted to studies of the stereochemical and conformational relations in these compounds[2-6] as well as the stereochemistry of nucleophilic substitution at the tetrahedral phosphorus atom in five-membered and six-membered phosphates and phosphonates[7].

For this reason, the results of preparative and stereochemical studies are used in the present review only to the extent that they are necessary for the interpretation of the specific features of the reactivities of cyclic phosphorus compounds. Cyclic derivatives of enediol phosphates, to the chemistry of which a recently published review is devoted[8], are not considered.

The only publication of the review type published in 1972, which discusses the characteristics of the reactivity of phosphorus-containing cyclic molecules, embraces the results of studies carried out mainly in the 1960s and deals with various types of phosphorus-containing heterocycles[9]. This review is concerned with experimental data published during the last ten years.

II. NUCLEOPHILIC SUBSTITUTION AT A TETRAHEDRAL PHOSPHORUS ATOM

1. 1,3,2-Diheterophospholans

The results of kinetic, stereochemical, thermochemical, and quantum-chemical studies and the investigation of the composition of the products of the hydrolysis of phosphorus(V) acids made it possible to formulate[10-13] the concept of trigonal-bipyramidal intermediates with the hydroxyphosphorane structure (the "hydroxyphosphorane concept" [12]), which constitutes the basis of the modern interpretation of the mechanism of nucleophilic substitution at a tetrahedral phosphorus atom. The use of the hydroxyphosphorane concept proved to be extremely fruitful in explaining the very marked acceleration (by a factor of millions) of the hydrolysis of five-membered cyclic phosphorus esters compared with their acyclic analogues.

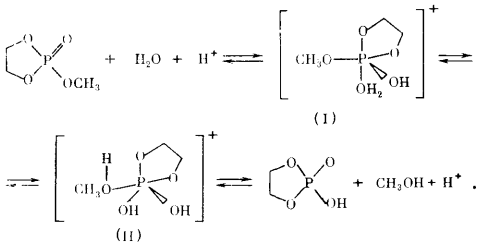
The hydrolysis of ethylene phosphate and its methyl ester takes place with the preferential opening of the five-membered ring; the exocyclic substitution product is formed in a smaller amount. However, both reactions are 10^6–10^8 times faster than the hydrolysis of trimethyl phosphate (see Westheimer's paper[10] and the literature quoted there). 2-Methoxy-2-oxo-1,2-oxaphospholan also hydrolyses very

rapidly and almost exclusively with the rupture of the endocyclic ester linkage, while the cyclic methyl tetramethylenephosphinate undergoes exocyclic hydrolysis at a rate close to that of the reactions of acyclic phosphorus esters.

Whereas the ease of the endocyclic rupture of the bonds on hydrolysis can be explained by the decrease of the strain in the five-membered rings within the framework of the $S_N2(P)$ concerted nucleophilic substitution mechanism[7,10], for the rapid exocyclic elimination of ester groups a satisfactory explanation has been obtained only on the hypothesis of an addition–elimination mechanism. When the nucleophile attacks the phosphorus atom, metastable trigonal-bipyramidal intermediates are formed whose stability and decomposition are regulated by the rules of the hydroxyphosphorane concept[12, 14, 15].

According to these rules, the addition of a nucleophile to the phosphorus atom leads to the formation of a phosphorane in which the attacking and leaving groups occupy axial (apical) positions. The strained five-membered rings containing the phosphorus atom then occupy one axial (*a*) and one equatorial (*e*) positions whereby a decrease of strain is achieved. The disposition of the ligands in the phosphorane obeys the polarity ("apicophilicity" [14]) rule—electron-accepting groups prefer *a*-positions and electron-donating groups prefer *e*-positions. Finally, the phosphoranes undergo ligand reorganisation (pseudorotation and permutation isomerisation), which is determined by the strain and apicophilicity rules[16–18].

From these standpoints, the rapid exocyclic hydrolysis of ethylene methyl phosphate in an acid medium can be readily accounted for by the conversion of the intermediate (I) into (II) as a consequence of pseudorotation, which results in the transfer of the leaving methoxy-group to the *a*-position[10,13]:

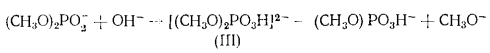


The endocyclic rupture of the bonds in the hydrolysis of the cyclic methyl propylenephosphinate is associated almost exclusively with the high energy barrier to the pseudorotation required to transfer the *e*-methoxy-group to the *a*-position; any permutation isomerisation causes the migration of an electron-donating endocyclic carbon atom to the *a*-position or the transfer of the five-membered ring to the *e*–*e*-position.

The slow hydrolysis of cyclic phosphinates is also due to the lack of pathways to the formation of low-energy hydroxyphosphoranes, because, as a result of pseudorotation, either the angle in the ring increases to 120° or one of the ring carbon atoms must substitute the oxygen atom in the *a*-position. The ring rupture on hydrolysis of ethylene methyl phosphate does not require pseudorotation, while substitution at the phosphorus atom can proceed via an intermediate resembling the transition state in a concerted S_N2 process†.

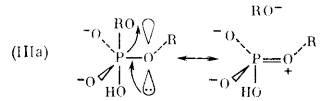
The main "driving force" of the rapid hydrolysis of ethylene phosphates is believed to be[10] ring strain. The heat of hydrolysis of ethylene phosphate exceeds by 20–25 kJ mol^{-1} that for acyclic phosphoric acid esters. On the other hand, the difference between the activation energies for the reactions of cyclic and acyclic phosphates reaches 40–45 kJ mol^{-1}, while the difference between the strain energies is 17–21 kJ mol^{-1} [19]; thus the high stabilisation (to the extent of almost 20–25 kJ mol^{-1}) of the cyclic transition state compared with the acyclic transition state (Fig. 1) cannot be explained solely from the standpoint of the strain in five-membered phosphorus-containing rings but is determined to a significant extent by stereoelectronic control or the orientation of the orbitals of the unshared electron pairs of the ligands[20].

Quantum-chemical calculations[20–22] of the potential energy cross-section of the model system

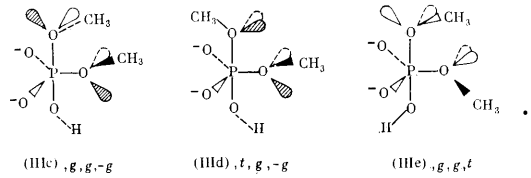


have shown that the reaction proceeds in two stages via intermediate (III) separated by activation barriers from the reactants and the reaction products. The energies of the transition state in both stages depend to a large extent on the conformations of the initial molecule of dimethyl phosphate and the molecule of the intermediate dimethoxyphosphorane and are subject to stereoelectronic control by the *e*-methoxy-group. This stereoelectronic effect is responsible for the selective weakening of the P–O ester linkages, which are in the *trans*-positions (antiperiplanar positions) relative to the unshared electron pairs of the adjacent oxygen atoms[21].

The nature of the stereoelectronic effect is explained within the framework of the anomeric effect[21,22]: the *a*-ester linkage P–OCH_3 is weakened in the molecule of compound (IIIa) for the *trans*-position (antiperiplanar position) of the orbital of the unshared electron pair of the *e*-oxygen atom. The *e*-ester linkage with the oxygen atom having the *trans*-unshared electron pair is stabilised. In other words, the resonance structure (IIIb) makes a significant contribution to the structure of the transition state:



The addition of OH^- to the *gauche*, *gauche*-conformer of dimethyl phosphate leads to the intermediate (IIIc) (*g*, *g*, -*g*), while the ester in the *gauche*, *trans*-conformation can form the phosphoranes (IIId) (*t*, *g*, -*g*) and (IIIe) (*g*, *g*, *t*).



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†Strictly speaking it is in principle impossible to draw a boundary between the $S_N2(P)$ and addition–elimination mechanisms in an endocyclic substitution reaction involving the inversion of the configuration at the phosphorus atom. Most probably in such situations we are dealing with the limiting cases of the same mechanism[7].

Calculation showed that the energy of the trigonal-bipyramidal transition state depends on the orientation of the *e*-ester linkage[20-22]. For the two-stage nucleophilic substitution process at the tetrahedral phosphorus atom, in which both stages are partly rate-determining[21], the rotation about the *e*-ester linkage during the reaction is significant. Whereas the *trans*-disposition of the unshared electron pair of the *e*-oxygen atom relative to the P–OH bond being formed is favourable for the attack stage [there is an energy gain of ~17 kJ mol^{-1} in structure (IIIe)], the *trans*-orientation of the unshared electron pair of the *e*-oxygen atom relative to the P–OCH_3 *a*-bond is required for the weakening of the bond between the phosphorus atom and the leaving group [there is an energy gain of ~45 kJ mol^{-1} in structures (IIIc) and (IIId)]. Only on rotation about the *e*-ester linkage in the course of the reaction can the stereoelectronic effect lower the activation barrier in both stages and hence the overall activation barrier. A necessary condition for such "stereoelectronic catalysis" [21] is the formation of intermediate pentacoordinate structures whose lifetime is sufficient for a single rotation.

In cyclic systems of the type of ethylene phosphate, where the favourable *trans*-disposition of the unshared electron pair of the *e*-oxygen and the *a*-ester linkage being ruptured is enforced in the potential hydroxy-phosphorane, the stereoelectronic effect ensures the stabilisation of the five-membered cyclic transition states (~25 kJ mol^{-1}) compared with the acyclic transition states, as shown in Fig.1.[20,21].

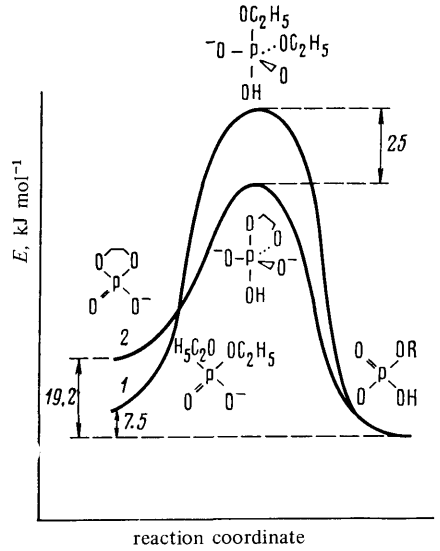


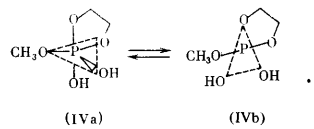
Figure 1. Reaction profiles of the OH^--catalysed hydrolysis of diethyl phosphate (curve *1*) and ethylene phosphate (curve *2*).[19]

The importance of the stereoelectronic control is confirmed by the considerable entropy contribution to the kinetic acceleration of the hydrolysis of five-membered cyclic phosphates[20]. Thus the entropy of activation for the latter is higher by almost 75 J mol^{-1} K^{-1} than for the acyclic ester[23]. Among all the possible conformations of the transition states in the hydrolysis of acyclic phosphates, only five undergo the interaction characteristic of *trans*-unshared electron pairs and the transition states of type (IIIc) or (IIId) are characterised by the lowest energy[20]. This requires the "freezing" of two rotational degrees of freedom about the acyclic ester linkages. The cyclic esters are already "frozen" in a suitable conformation with a low energy which is reflected in the difference between the activation entropies. The arrest of the free rotation about the ester linkages is responsible for the low negative entropies of activation for the acyclic esters (−143– −161 J mol^{-1} K^{-1}). In order to compensate for this unfavourable entropy, the stereoelectronic enthalpy gain must indeed be significant[20].

In the general case the reactivity of 1,3,2-diheterophospholans in nucleophilic substitution reactions at the tetrahedral phosphorus atom, the stereochemistry of these reactions (the retention or inversion of the configuration at the phosphorus atom), and the nature of the bond rupture (endocyclic or exocyclic) depend on many causes: on the presence or absence of catalysis (neutral, acid, or alkaline hydrolysis), on the type of heteroatoms linked to phosphorus, on the nature of the nucleophile and the leaving group, on the influence of the substituents in the five-membered ring, and on the nature of other electrophilic centres in the substrate molecule.

Kinetic studies and the investigation of the composition of the products of the hydrolysis as a result of the exocyclic and endocyclic substitution of the ester groups of ethylene methyl phosphate over a wide pH range in the medium[24] showed that the rate of reaction (Fig.2) and the *exo*/*endo* ratio (Fig.3) depend markedly on the nature of the catalysis.

If the ring rupture does not require pseudorotation, then the elimination of the methoxy-group is possible only after the conversion of the intermediate (IVa) into (IVb):



(IVa) (IVb)

In acid hydrolysis the intermediate phosphorane (IVa) is protonated by the *a*-oxygen atom[24], which prevents the conversion of compound (IVa) into (IVb), because the electronegative oxonium oxygen atom then migrates to the *e*-position. Therefore, with increase of the acidity of the medium, the fraction of the products formed as a result of ring rupture increases (Fig.3); the rate of reaction then varies linearly with the acid concentration (the left-hand branch of the curve in Fig.2).

The increase of the content of the cyclic product in dilute solutions (up to 50%, Fig.3) can be associated with the rate-determining pseudorotation in these instances[24]. In the regions where the pH is close to the value for a neutral medium, the rate of reaction is much lower and the fraction of the cyclic product reaches 25%.

In weak alkalis the intermediates exist in a monoanionic form with an anionic *e*-oxygen atom and pseudorotation giving rise to the anion of hydroxyphosphorinane (IVb) is in principle possible. The predominance of the endocyclic rupture in this instance can be accounted for by the fact that the rate of abstraction of the endocyclic *a*-oxygen atom is much higher than the rate of pseudorotation[24].

In a strongly alkaline solution the increase of the fraction of the cyclic product is most probably associated with the favourable energy of the permutation isomerisation of the

dianion of phosphorane (IVa) with an anionic α-substituent to the anion of the acid (IVb) in which both negatively charged oxygen atoms are located in the e-positions.

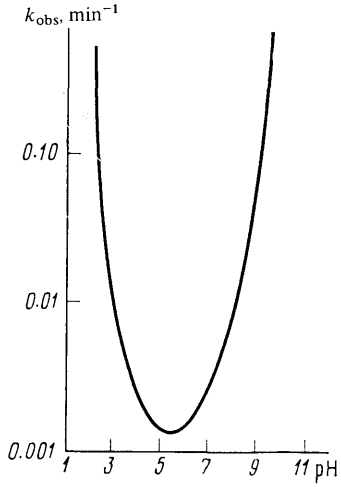


Figure 2. The rate of hydrolysis of ethylene methyl phosphate at 298 K.[24]

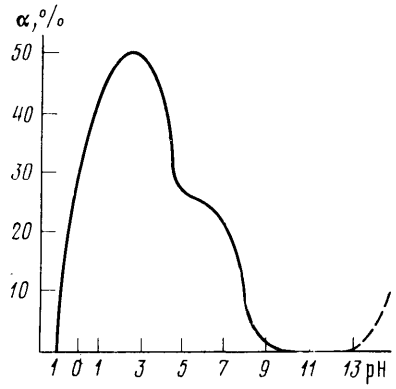


Figure 3. The pH profile of the hydrolysis products of ethylene methyl phosphate in water at 298 K;[24] α is the content of products formed as a result of exocyclic substitution.

The retention of the 1,3,2-diheterophospholan ring on hydrolysis and alcoholysis is observed fairly frequently [compounds (V), (VI), (VIII), (IX), (XIV), (XVIII), (XX), and (XXV) in Table 1]. 1,3,2-Dioxaphospholans and their benzo-derivatives react in a neutral solution with a limited amount of water with the preferential elimination of exocyclic groups [compounds (XIV) and (VIII) in Table 1];[25-27] the hydrolysis of the benzodiheterophospholan ring is a secondary process. On the other hand, there are data[28] indicating the exceptional hydrolytic instability of the benzodioxaphospholan ring. Thus the alcoholysis of phenyl phenylene phosphate (XVI) with ring opening under the influence of isobutyl alcohol takes place very rapidly at room temperature; 2-ethylpropanol reacts in 5 min, while 2,4-dimethyl-3-pentanol reacts in 2 h. After standing for a long time at room temperature, the acyclic alcoholysis products recyclise to alkyl phenylene phosphates. An analogous situation has been observed in the reaction of the phenylene phosphate anion (XV) with α-chymotrypsin[29].

These results show that both the ring opening products and the exocyclic substitution products can be formed as a result of secondary reactions and the assessment of the nature of the substitution (exocyclic or endocyclic) must be performed with some caution.

The hydrolysis and methanolysis of acyl ethylene phosphate (VII) also proceed with retention of the ethylene phosphate ring[30]. It is striking that nucleophilic substitution is in this case directed to the phosphoryl and not the carbonyl centre, which is apparently due to the unfavourable energetic features of the intermediate with a pentacoordinate phosphorus atom, analogous to compound (I). The rate of reaction of compound (VII) is much higher than that of its acyclic analogue—acetyl dimethyl phosphate.

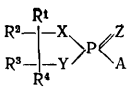
Preferential attack by nucleophiles on the phosphoryl rather than the carbonyl group has been observed in the alcoholysis, acidolysis, and aminolysis of 2,4-dioxo-1,3,2-diazaphospholans[31]. On the other hand, six-membered and acyclic acyl phosphates react with nucleophiles preferentially or fully via the acylation mechanism[32].

The relative ease of dissociation of the exocyclic and endocyclic ester linkages depends significantly on the degree of substitution of the ring carbon atoms. For example, in neutral media ethylene methyl phosphate hydrolyses almost completely with ring opening[24], while methyl tetramethylethylene phosphate (VI) forms methyl pinacolphosphoric acid under these conditions[33]. Alkaline hydrolysis takes place as a rule almost exclusively with the endocyclic rupture of ester linkages[24,33]. However, under these conditions too the dioxaphospholan fragment is ruptured preferentially at the P–O bond adjoining the least substituted carbon atom. Thus the endocyclic hydrolysis of compound (XVIII) takes place to the extent of 50% with rupture of the ester linkage involving the secondary carbon atom and to the extent of 20% with the rupture of the linkage involving the tertiary carbon atom[34].

It is most likely that the latter feature is associated with the fact that, on formation of the trigonal-bipyramidal intermediate, the oxygen atom linked to the least substituted (less electropositive and hence more apicophilic) carbon atom occupies preferentially the a-position for the a–e disposition of the five-membered ring. Naturally, this difference between the electronegativities of the ring carbon atoms is small and for this reason both ester linkages are ruptured.

Other conditions being equal, an increase in the number of alkyl substituents in the 1,3,2-diheterophospholan ring increases the hydrolytic stability of the cyclic skeleton of the molecule[35,36]. For example, it is known that the tendency of 1,3,2-dioxaphospholans to undergo reversible oligomerisation with ring opening is much greater for the unsubstituted cyclic compounds. The introduction of even one alkyl substituent at the ring carbon atoms sharply increases the stability of the molecules[37,38].

The greater stability of the substituted five-membered rings in hydrolysis reflects the tendency, common to small rings, to become stabilised with increase of the number of substituents[39,40], particularly in the presence of *gem*-dialkyl groups (the Ingold–Thorpe effect[41,42]).

Table 1. The rupture of bonds in the hydrolysis and alcoholysis of 1,3,2-diheterophospholans of the type  .

No.	Compound								Reaction conditions	α, %	β, %	References
	R_1	R_2	R_3	R_4	X	Y	Z	A				
(V)	H	H	H	H	O	O	O	OCH_3	H_2O, 298 K, pH 2*	55	45 (P—O)	[10, 24]
(VI)	CH_3	CH_3	CH_3	CH_3	O	O	O	OCH_3	dioxan–H_2O (1 : 1), t_{room}, 0.1 M NaOH**		100 (P—O)	[31]
(VII)	H	H	H	H	O	O	O	$OCOCH_3$	H_2O, t_{room}, 15 s	100	—	[33]
(VIII)	—*o*-C_6H_4—				O	NH	O	OC_6H_5	THF, 3 M H_2O, t_{room}	85	—	[26]
(IX)	—*o*-C_6H_4—				O	O	O	HC_6H_5	ditto	64	—	[26]
(X)	—*o*-C_6H_4—				O	S	O	OC_6H_5	»	30	45 (P—S)	[26]
(XI)	—*o*-C_6H_4—				S	NH	O	OC_6H_5	»	8	0.7 (P—N); 78 (P—S)	[26]
(XII)	—*o*-C_6H_4—				NH	NH	O	NHC_6H_5	»	—	***	[26]
(XIII)	—*o*-C_6H_4—				NH	NH	O	$CH_2C_6H_5$	»	—	***	[26]
(XIV)	—*o*-C_6H_4—				NH	NH	O	OC_6H_5		27	51 (P—N)	[26]
									THF, 1 M CH_3OH, 2 h	48	17 (P—N)	[27]
(XV)	—*o*-C_6H_4—				O	O	O	O^-	α-chymotrypsin, pH 7, 298 K	—	100 (P—O)	[29]
(XVI)	—*o*-C_6H_4—				O	O	O	OC_6H_5	THF, 3 M H_2O, t_{room}****	68	21 (P—O)	[26]
(XVII)	H	H	H	H	NCH_3	O	O	OCH_3	H_2O, 0.01–0.005 M NaOH	0	60 (P—O); 40 (P—N)	[34]
(XVIII)	H	CH_3	H	H	O	O	O	$N(CH_3)_2$	ditto	30	20 (P—X); 50 (P—Y)	[34]
(XIX)	H	H	H	H	NC_6H_5	O	O	OCH_3	»	0	100 (P—O)	[34]
(XX)	H	H	H	H	NC_6H_5	O	O	OC_6H_5	»	91	4 (P—O); 5 (P—N)	[34]
(XXI)	H	H	H	H	NCH_3	O	O	C_6H_5	»	0	100 (P—O)	[43]
(XXII)	H	H	H	H	NC_6H_5	O	O	C_6H_5	»	0	100 (P—N)	[43]
(XXIII)	H	CH_3	H	C_6H_5	NCH_3	O	O	CH_3	RONa or HCl in ROH, t_{room}	0	100 (P—N)	[45]
(XXIV)	H	CH_3	H	C_6H_5	CH_3	O	Se	CH_3	ROH, t_{room}	0	100 (P—N)	[46]
(XXV)	H	CH_3	H	C_6H_5	CH_3	O	S	$N(C_2H_5)_2$	$NaOCH_3$ in CH_3OH*****	0	100 (P—N)	[47]
(XXVI)	H	CH_3	H	C_6H_5	NCH_3	O	S	CH_3	NaOR in ROH	—	100 (P—N)	[47]
(XXVII)	H	CH_3	H	C_6H_5	NCH_3	S	S	CH_3	ditto	—	100 (P—N)	[50]
(XXVIII)	H	CH_3	H	C_6H_5	NCH_3	S	O	OC_2H_5	»	—	100 (P—N)	[50]
(XXIX)	H	H	H	H	O	S	O	C_6H_5	0.1 *N* Na_2CO_3 in H_2O, 298 K	0	100 (P—O)	[55–57]
(XXX)	H	H	H	H	O	S	O	C_6H_5	ditto	0	100 (P—O)	[55–57]
(XXXI)	H	H	H	H	O	S	O	OCH_3	»	0	100 (P—S)	[55–57]

Note. α and β are the amounts of products formed as a result of the exocyclic and endocyclic ruptures respectively; the bond ruptured is indicated in brackets against the values of β.

*α = 17% and β = 83% (P—O) at pH 7 and α = 1% and β = 99% at pH 13 were obtained. **α = 100% was obtained for the 1:1 1,2-dimethoxyethane–H_2O system. ***Reaction does not occur. ****α = 10% and β = 90% (P—O) were obtained for the following conditions: $(CH_3)_2CHCH_2OH$, fast; $(C_2H_5)CHOH$, 5 min; $[(CH_3)_2CH]_2CHOH$, 2 h. *****t_{ki} = 20 min and α = 20% for the system comprising 3 moles of aqueous HCl in acetone.

If readily removed exocyclic substituents, for example aryloxy-substituents, are linked to the phosphorus atom, then the ring is retained and the rate of hydrolysis is described satisfactorily by the Hammett equation when the substituent in the leaving group is varied[44].

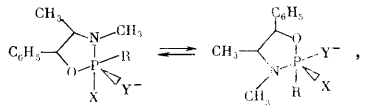
In the presence of unlike heteroatoms in the 1,3,2-diheterophospholan ring, nucleophilic substitution results in the preferential rupture of the bond between the phosphorus atom and the more apicophilic heteroatom or group. Alkaline hydrolysis of the cyclic phosphoramidate (XIX) and of the phosphonate (XXI) leads exclusively to the rupture of the endocyclic P—O bond, because the oxygen atom is more apicophilic than the NC_6H_5 group[34,43]. However, according to other data[45–47], the relative apicophilicities of the atoms can change following their incorporation in the heterocycle. The exclusive P—N rupture on alcoholysis of oxazaphospholans (XXIII)–(XXVIII) is attributed to the greater apicophilicity of the endocyclic nitrogen atom and the oxygen atom[45–47,51].

Thus the characteristic feature of cyclic aminoesters of phosphorus acids is the ease of the cleavage of the phosphamide linkages under the conditions of alkaline hydrolysis and alcoholysis. The alkaline hydrolysis of the phosphoramidates (XVII) and (XVIII) proceeds to the extent of 40 and 30% respectively with substitution of the amino-groups[34]. The base-catalysed hydrolysis of the phosphoramidate (XXII) [43] and the alcoholysis of the cyclic phosphorus derivatives (XXII)–(XXVI) based on (-)-ephedrine proceed wholly with dissociation of the P—N bond[45–48]. The rupture of the amide rather than the less stable thioester linkage has been observed in the hydrolysis[49] and alcoholysis[50] of the thiazaphospholans (XXVII) and (XXVIII), but the hydrolysis of compound (XI) in a neutral medium proceeds mainly with rupture of the P—S bond[26], while the exocyclic substitution of the phenoxy-group competes with the cleavage of the labile P—N bond in the oxathiaphospholan (X).

On the other hand, the acyclic amidoesters of phorphorus acids hydrolyse in alkaline solutions exclusively with liberation of the alcohol[34,44,51]. It has been suggested[52] that this difference is associated with the change in the nature of the P—N bond when it is incorporated in a rigid five-membered ring. The amino-group in acyclic phosphoramidates can "choose" the conformation in which there is maximum overlap of the orbital of the unshared electron pair of the nitrogen atom with the d orbitals of phorphorus, which strengthens the phosphamide linkage and lowers the electrophilicity of the phosphorus and the basicity of the nitrogen. When the P—N bond incorporated in a five-membered ring and the overlap weakens and hence the basicity of the nitrogen, the electrophilicity of the phosphorus, and the lability of the phosphamide linkage increase.

However, the interaction of alkyl(aryl)phosphonamidate, phosphinoselenoate, and phosphonamidothioate derivatives (XXIII), (XXIV), (XXVI), and (XXVII) of (-)-ephedrine

and (+)-pseudoephedrine with organolithium and organomagnesium compounds takes place with dissociation of the P–O and P–N bonds, the ratios of the reaction products depending both on the nature of the nucleophile and on the steric structure of the ring[7,51–53]. The difference from the reactions with oxygen-centred nucleophiles is associated with different barriers to the transformations of the intermediates (XXXII) and (XXXIII):



(XXXII) (XXXIII)

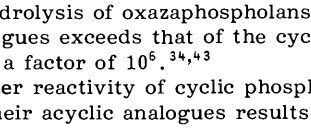
R=CH_3, C_6H_5; Y=O, S; X=OR, R, C_6H_5.

When X = OR, the pseudorotation (XXXII) ⇌ (XXXIII) is hindered, because the apicophilicity of the alkoxy-substituents is somewhat greater than that of the methyl or phenyl group; in such phosphoranes the α-elimination of the amino-group takes place. The apicophilicities of the group X (X = alkyl or aryl) and the equatorial substituents R are similar and pseudorotation and the subsequent heterolysis of the P–O bond compete with the endocyclic dissociation of the P–N bond. Furthermore, in many instances the nucleophile X can attack approximately equally readily the P–O and P–N groups from the rear. The interconversion energy of the intermediates is influenced by the nature and steric disposition of the ring substituents. In other words, there is a fine balance of all the factors which determine the nature of the rupture and the stereochemistry of the reaction involving substitution by organometallic nucleophiles[53].

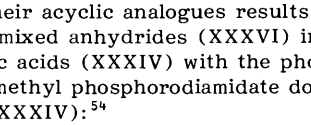
Acid hydrolysis of phosphoramidates takes place with substitution of the amino-group, because the nitrogen atom, being the most basic centre, is the first to be protonated, while the ammonium substituent is very readily eliminated. The insignificant contribution (5%) of the P–N dissociation in the hydrolysis of the phosphoramidate (XX) has been explained by general acid catalysis[44]. However, the exclusive P–N dissociation in the *N*-phenylphosphonate (XXII), where the nitrogen is less basic than in the *N*-methyl derivative (XXI), conflicts with this hypothesis. In order to account for this contradiction, a square-pyramidal structure of the intermediate has been proposed[43]. The full amides (XII) and (XIII) are not hydrolysed in a neutral medium.

The rate of hydrolysis of oxazaphospholans as well as their dioxa-analogues exceeds that of the cyclic phosphoramidates by a factor of 10^6.[34,43]

The much higher reactivity of cyclic phosphoramidates compared with their acyclic analogues results in the ready formation of the mixed anhydrides (XXXVI) in the reactions of arylphosphoric acids (XXXIV) with the phosphoramidate (XXXVI), while methyl phosphorodiamidate does not react with compound (XXXIV):[54]

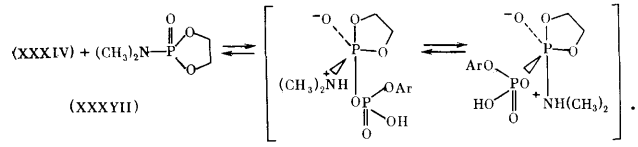


(XXXIV) (XXXV)



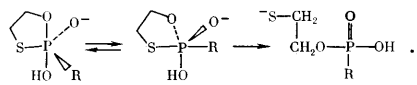
(XXXVI)

It is of interest that ethylene *N,N*-dimethylphosphoramidate (XXXVII) is also inert in this reaction; this is apparently associated with the unfavourable energetic features of the intermediate (XXXVIII) (in which the ammonium group characteristically assumes an equatorial position) or its rotational isomer (XXXIX) (where the electronegative hydroxyphosphoryl group is equatorial):



(XXXVII) (XXXVIII) (XXXIX)

A difference between the types of endocyclic dissociations has also been established in the series of oxathiaphospholans (XXIX)–(XXXI).[55–57] The alkaline hydrolysis of ethylene methyl phosphorothiolate (XXXI) involves, like that of the acyclic thiolo-esters of phosphorus acids[56], the substitution of the thioester group with formation of compound (XLII), while the hydrolysis products of the phosphorothioate anion (XXIX) and of the phosphonothioate (XXX) are the β-hydroxyethyl thiolo-esters of the corresponding acids. This can be explained by the different capacities of the intermediates (XL) for pseudorotation in the presence of different substituents R:



(XL) (XL1) (XLII)

A necessary condition for the P–S dissociation is the transformation of the bipyramid (XL) into (XLI), which is allowed only for R = OCH_3. Such pseudorotation is difficult for R = O [compound (XXIX)] and C_6H_5 [compound (XXX)] (the less apicophilic groups should migrate to the α-position) and it cannot compete with the endocyclic dissociation of the P–O α-bond.

2. 1,3,2-Diheterophosphorinanes

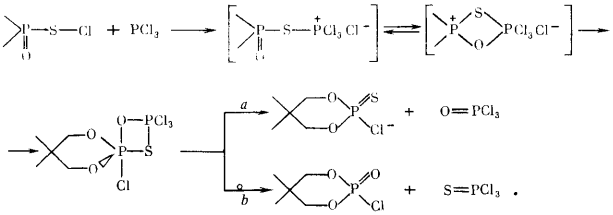
Nucleophilic substitution at the tetrahedral phosphorus atom incorporated in a six-membered 1,3,2-diheterophosphorinane ring does not involve a striking difference between the rates of reaction of cyclic and acyclic phosphorus acid esters of the kind observed in the series of 1,3,2-diheterophospholans. In contrast to the five-membered phosphorus-containing heterocycles, the six-membered heterocycles are more stable and in the presence at the phosphorus atom of a readily eliminated exocyclic group the substitution takes place with retention of the ring. The rate of exocyclic hydrolysis is very close to that of the analogous reactions of acyclic phosphates[7,10,58,59]. This is most probably associated with the absence of angular strain in the six-membered rings and with the similarity between the structure of the trigonal-bipyramidal intermediate, formed as a result of the addition of the nucleophile to the phosphorus atom, and the structure of the transition state in $S_N2(P)$ reactions (at any rate, in exocyclic nucleophilic substitution occurring with inversion of the configuration at the phosphorus atom[60]).

The formation of such intermediates presupposes that the six-membered ring is in the diequatorial position, which is energetically more favourable[11,12] than the *a–e* positions.

However, the arrangement in the phosphorane bipyramid of the six-membered rings in which a heteroatom is linked to the phosphorus atom is determined by the effect of the orientation of the unshared electron pairs of the heteroatom. The structure with the *a*–*e*-ring in the boat conformation has the lowest energy[7,60,61,62]. This conclusion agrees with the results of the X-ray diffraction analysis of the phosphorane containing the oxazaphosphorinane ring[61].

It has also been suggested that structures with the *e*–*e* and *a*–*e* disposition of the diheterophosphorinane ring have comparable energies[63,64]. On the other hand, the authors of recent investigations into the stereochemistry of nucleophilic substitution reactions of organophosphorus carbohydrate derivatives[65] question this claim on the grounds that the *a*–*e* disposition of the dioxaphosphorinane rings is thermodynamically preferred. This last factor is believed to be responsible[7,65] for the appreciably higher (by a factor ≥10) rate of ring opening in six-membered cyclic phosphates than was believed previously[10,58].

The *e*–*e* disposition of the six-membered ring is apparently the only one possible in the intermediate compounds in the reactions of cyclic phosphorylsulphenyl chlorides with phosphorus trichloride[66]. The reaction proceeds via the successive formation of quasi-phosphonium intermediates. The dicyclic phosphorane formed subsequently can decompose with abstraction of an oxygen atom from the four-membered ring or after the pseudorotation of the sulphur atom:



It is striking that acyclic phosphonosulphenyl chlorides undergo only deoxidation on treatment with phosphorus trichloride (pathway *a*). The lifetime of the phosphorane intermediate formed from the acyclic substrate is probably insufficiently long for the pseudorotation necessary for the occurrence of desulphurisation (pathway *b*).

It has been shown in a number of instances that, of the two enantiomeric 1,3,2-diheterophosphorinanes, the stereoisomer with the *a*-disposition of the P=X groups hydrolyses at a higher rate[20,60,67,68]. Thus 2-aryloxy-2-oxo-*trans*-5,6-tetramethylene-1,3,2-dioxaphosphorinanes with the P=O *e*-group hydrolyse 4–17 times more slowly than their epimers[60]. The difference between the energies of the ground states of the phosphorus-containing cyclic structures is responsible for this difference in behaviour: the P=O group occupies preferentially the *e*-position and the energy of isomers with this structure is lower by 6–8 kJ mol^{-1}. The difference between the energies of the transition states in these systems is very small (~0.8 kJ mol^{-1}). A similar difference between the reactivities of the stereoisomers has been observed in the hydrolysis of uridine 3,5-phosphates, where the difference between the energies of the ground states is ~3 kJ mol^{-1}.[69]

Endocyclic rupture occurs in 2-alkyl(aryl)-1,3,2-diheterophosphorinanes, in which the substitution of the exocyclic groups is impossible[7]. In those cases where a group difficult to eliminate is linked to the phosphorus atom, exocyclic cleavage competes with the ring opening[70,71]. In the series of *p*-substituted 5-chloromethyl-5-methyl-2-oxo-(phenoxy)-1,3,2-dioxaphosphorinanes the influence of the *p*-substituents on the reaction rate is not very significant, which is reflected in the constant $\rho = 0.95$ in the Hammett equation[7].

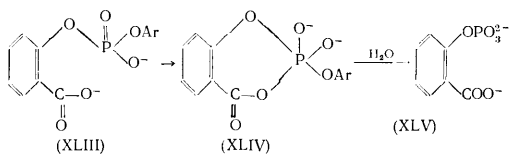
It has been suggested that the trigonal-bipyramidal intermediates formed initially in reactions with retention of the configuration at the phosphorus atom undergo pseudorotation[60,71,72]. An alternative explanation involves the formation of square-pyramidal intermediate structures[69,70].

As in the series of five-membered cyclic phosphates, the nature of the endocyclic dissociation of the phosphorus–heteroatom bonds in 1,3,2-diheterophosphorinanes depends on the nature of the heteroatoms in the ring and the substituents at the ring carbon atoms. The acid-catalysed hydrolysis of 1,3,2-oxazaphosphorinanes proceeds with dissociation of the P–N bond[7,73–75], while in reactions involving alkaline hydrolysis the stability of the P–N bond is intermediate between that of the stable acyclic amidoesters of phosphorus acids and that of the labile 1,3,2-oxazaphospholans[7,76,77].

The relative ease of the P–O and P–S dissociations in 1,3,2-oxathiaphosphorinane derivatives depends on the nature of the exocyclic substituents. Thus 2-ethoxy-2-oxo-1,3,2-oxathiaphosphorinanes undergo P–S cleavage in the CH_3ONa–CH_3OH system, while in the analogous methyl phosphonates the P–O bond is ruptured[7,70]. This result indicates an appreciable difference between the cyclic and acyclic phosphorus thiolo-compounds. As already stated, the acyclic thiolo-esters of phosphorus acids hydrolyse in the first place at the thioester linkage in all cases.

The influence of the substituents at the ring carbon atoms on the rate of nucleophilic substitution at a phosphorus atom incorporated in a six-membered ring has been studied in only a few instances[78–82]. The ester linkage with a secondary carbon atom is more labile in 1,3,2-dioxaphosphorinanes than the similar bond with a tertiary carbon atom[70]. The ease of ring opening in carbohydrate derivatives depends on the nature of the initial glucoside. In *trans*-joined 1,3,2-dioxaphosphorinanes derived from glucose the ring opening under the influence of Grignard reagents takes place under mild conditions; the *cis*-joined phosphate esters of galactose are fairly inert and react only after refluxing in benzene for 96 h.[78]

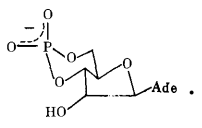
The acceleration of the reaction by a factor of 10^7–10^8 in the hydrolysis of aryl 2-carboxyphenyl phosphates (XLIII) in the region of pH 5, in which the *o*-carboxy group is ionised, has been explained by the intermediate formation of the phosphorane (XLIV), whose decomposition is responsible for the large effect in the formation of the monoaryl phosphate (XLV):[79]



(XLIII) (XLIV) (XLV)

The combined thermochemical, quantum-chemical, and stereochemical study[80–82] makes it possible to explain why the enthalpy of hydrolysis of six-membered cyclic adenosine 3′,5′-monophosphates (XLVI) is higher by ~33 kJ mol^{-1}

compared with trimethylene phosphate:



(XLVI)

It was established that ~21 kJ mol^{-1} corresponds to the strain induced by the ribofuranoside component of the molecule, *trans*-condensed relative to the phosphorus-containing ring. A definite proportion of the enthalpy difference (4.0–8.5 kJ mol^{-1}) is associated with the enforced fixation of the 5-alkoxy-substituent in the unfavourable *e*-position, which destabilises the system. Finally, 4–8 kJ mol^{-1} is due to the difference between the solvation energies of the reactants and products.

It has been shown that the enthalpies of hydrolysis of diethyl phosphate (~10.5 kJ mol^{-1}) and trimethylene phosphate (~16 kJ mol^{-1}) do not differ significantly[80].

The enthalpy of hydrolysis of cyclic phosphates can serve as a measure of the stability of the molecule in the synthesis of cyclic phosphates, for example, from the corresponding phosphorus acid dichlorides and diols[83]. The threshold of the enthalpy of hydrolysis above which cyclic phosphates lose their stability under the usual conditions (polymers and decomposition products are formed instead of the expected cyclic esters) is ~25 kJ mol^{-1}.

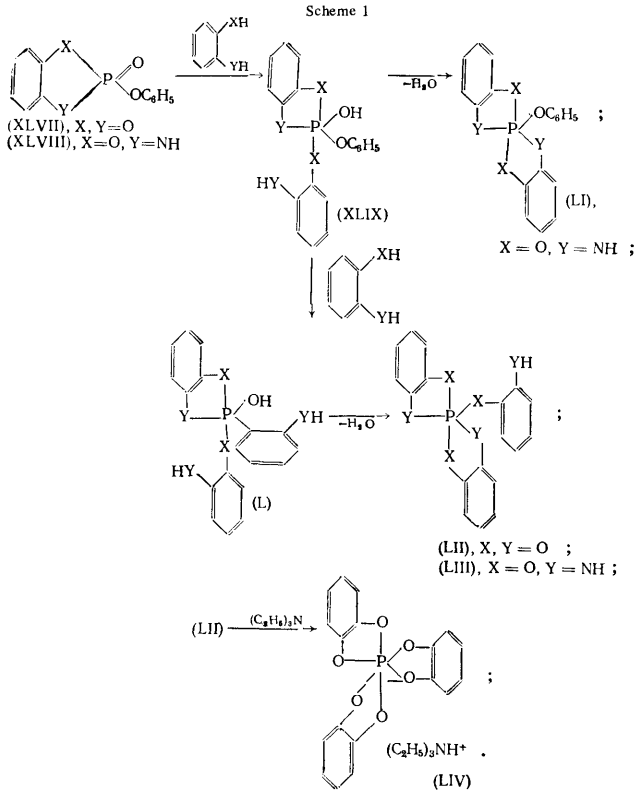
3. Nucleophilic Reactions with Increase of the Coordination Number of Phosphorus Atoms

A serious argument in support of the hydroxyphosphorinane concept was the detection of hydroxyphosphoranes formed in the course of the intramolecular and intermolecular nucleophilic substitution at a tetrahedral phosphorus atom. Direct evidence for the formation of hydroxyphosphorinane was obtained for the first time in a study of the interaction of phenyl phosphorodichloridate with catechol and *o*-aminophenol in the presence of triethylamine[84].

It was found that in the first case a salt of hexacoordinate phosphorus (LIV) is formed instead of the expected phenyl phenylene phosphate (XLVII). *o*-Aminophenol gives rise to small amounts of compounds (LI) and (LIII) with a phosphorane structure together with compound (LIV). The reaction of compound (XLVII) with catechol and *o*-aminophenol leads to analogous products. The formation of organophosphorus compounds with an increased coordination number is possible only as a result of the intermediate formation of the hydroxyphosphoranes (XLIX) and (L) via Scheme 1.

It was established subsequently that the formation of the phosphorane (LIV) is extremely characteristic of the reactions of catechol with 2-halogenobenzo-1,3,2-oxaphospholans containing an atom of tricoordinate, tetracoordinate, or pentacoordinate phosphorus in the ring[85,86].

Scheme 1



(XLVII), X, Y=O
(XLVIII), X=O, Y=NH

(XLIX)

(LI), X = O, Y = NH ;

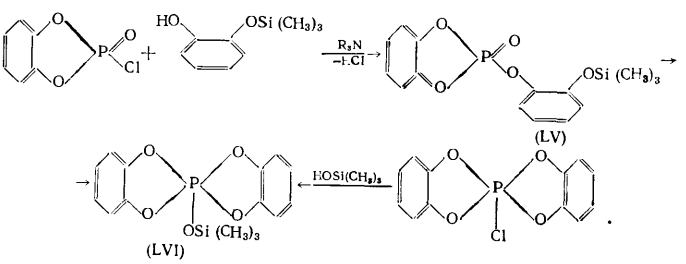
(L)

(LII), X, Y = O ;
(LIII), X = O, Y = NH ;

(LII) $\xrightarrow{(C_2H_5)_3N}$

(LIV)

The reaction of phenylene phosphorochloridate with *o*-trimethylsiloxyphenol[87] in the presence of triethylamine leads to the phosphate (LV), which fully isomerises in aprotic solvents to spirotrimethylsiloxydiphenylenephosphorane (LVI); the latter can be obtained by specific synthesis from spirochlorodiphenylenephosphorane and trimethylsilanol:

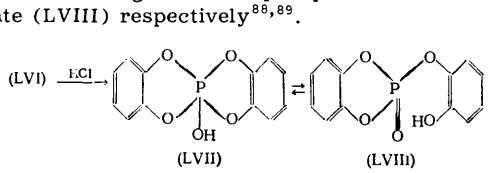


(LV)

(LVI)

The possibility of such silyl transfer apparently arises from the greater stability of the $(RO)_4P-O-SiR'_3$ system compared with $Ar-O-SiR'_3$.[87]

When silylphosphorane (LVI) reacts with anhydrous hydrogen chloride, a crystalline substance is formed, exhibiting features of a dynamic equilibrium in aprotic solvents: two signals in ^{31}P NMR spectra at −27 and +7 p.p.m. were assigned to the phosphorane (LVII) and the phosphate (LVIII) respectively[88,89].



(LVI)

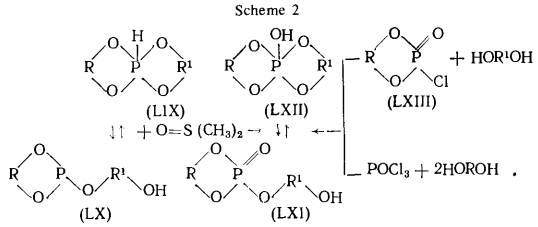
(LVII) (LVIII)

In the crystalline state this substance consists of the phosphate (LVIII). In acetonitrile at 225 K, the ratio of the quinquevalent and quadrivalent phosphorus forms $P^{V}:P^{IV}$ = 1.5:1, while in acetone it is 3:1.

The reaction of compound (LVIII) with diazomethane leads exclusively to methoxyspirodiphenylenephosphorane. Acylation yields 80% of 2-acetoxyphenyl phenylene phosphate and 20% of acetoxyspirodiphenylenephosphorane.

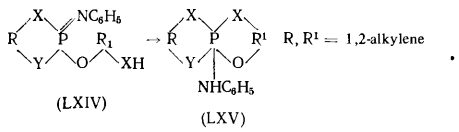
The phosphate–phosphorane tautomerism has been observed in the products of the oxidation of the prototropic system (LIX) ⇌ (LX) with dimethyl sulphoxide and also in the cyclic phosphates formed when alkylene phosphorochloridates (LXIII) or phosphoryl chloride react with diols[90–93] via Scheme 2:

Scheme 2

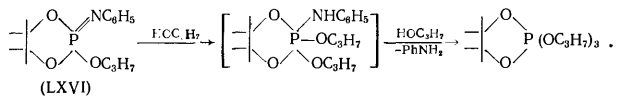


An increase in the number of substituents in five-membered rings and an increase of their electron-accepting capacity stabilise the phosphorus(V) form[93]. The equilibrium (LXI) ⇌ (LXII) shifts towards the hydroxyphosphorane with increase of the basicity of the medium[91].

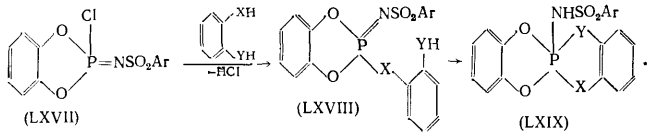
The intramolecular proton transfer from the functional group in the γ-position to the heteroatom in the P=X bond has been demonstrated in five-membered cyclic phosphorimidates[94,95]:



Although the phosphorimidate (LXIV), formed in the reaction of phosphites of type (LX) with phenyl azide, could not be identified, its transformation into compound (LXV) is modelled by the addition of an alcohol to the imide linkage of the phosphorimidate (LXVI):

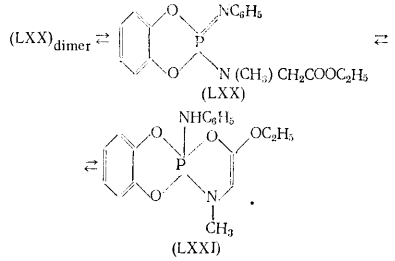


The interaction of 2-acylimino-2-chloro-4,5-benzo-1,3,2-dioxaphospholan (LXVII) with catechol, *o*-phenylenediamine, and *o*-aminophenol proceeds via a stage involving the formation of the phosphorimidate (LXVIII) with the subsequent intramolecular prototropic isomerisation to the spirophosphorane (LXIX):[96,97]

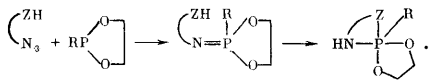


It was shown that the reactivity of the phosphorimidochloridate (LXVII) is higher than that of acyclic dialkoxychlorophosphazo-compounds[98].

An interesting case of reversible prototropic isomerisation was observed in the thermolysis of phosphoramidimidate (LXX), which is dimerised under the usual conditions (see below). When the dimer of the phospholan (LXX) is heated, it is converted into the monomeric form and then isomerises to the aminospirophosphorane (LXXI) with intramolecular proton transfer to the phosphorimide nitrogen atom[99]:

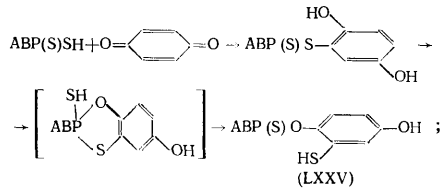


An analogous intramolecular prototropic process has been used to synthesise stable cyclic spirophosphoranes by the reaction of phosphites with bifunctional azides[100]:



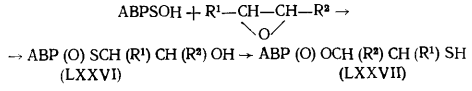
The driving force of the intramolecular nucleophilic attack by the nucleophilic functional group in the γ-position on the phosphorus atom is spirocyclisation, leading to stable spirophosphoranes[14,89,94,101]. Acyclic organophosphorus compounds with a 2-hydroxy(amino, mercapto)ester group do not form hydroxyphosphoranes which would be sufficiently stable for identification[101]. This reflects the well-known sequence based on the decrease of the stability of phosphoranes; spirocyclic > monocyclic > acyclic.[102]

The isomerisation of *S*-(2-hydroxyalkyl) esters of phosphorus thioacids probably also proceeds via the hydroxy(mercapto)phosphorane stage. At any rate, the much greater ease of the isomerisation of the esters of cyclic ω-hydroxy(mercapto)phosphates compared with the acyclic compounds can be associated with the more favourable energetic features of the bicyclic intermediates[103–105]. Thus the product of the addition of alkylene phosphorodithioic acids to *p*-quinone isomerises to the corresponding phosphoromonothioate (LXXV) so rapidly that under the usual conditions the adducts (LXXIII) and (LXXIV) cannot be isolated, while *O,O*-dialkyl *S*-(2,5-dihydroxyphenyl) phosphorodithioates (LXXII) isomerise only at an elevated temperature[103]:



(LXXII)), A=B=Alko (LXXIII), AB=OC $(CH_3)_2C(CH_3)_2O$ (LXXIV), AB=$OCH_2C(CH_3)_2CH_2O$.

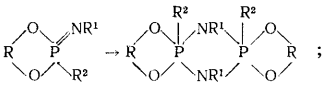
The stability of the products of the addition of phosphorus monothioacids to oxirans depends greatly on the nature of the substituents at the phosphorus atoms: whereas the acyclic *S*-(2-hydroxyalkyl) phosphorothioates (LXXVI) are fairly stable at room temperature, in the case of five-membered 2-hydroxyalkyl derivatives only the isomerisation products were detected—2-(2′-mercaptoalkyl)-2-oxo-1,3,2-dioxaphospholans (LXXVII). 2-Hydroxyalkyl phosphorothioates of the 1,3,2-dioxaphosphorinane series (LXXVI) can be detected by ^{31}P NMR.[104]



where AB = 1,2-dihydroxyalkylene. Evidently, the intermediate hydroxyphosphoranes with two five-membered rings have a lower energy than the intermediates with five- and six-membered rings, which are in turn more stable than the monocyclic phosphoranes.

It is striking that *S*-(3-hydroxyalkyl) phosphorothioates—the products of the addition of five-membered cyclic phosphoromonothioic acid to oxetans—are readily converted in ethereal solution into 3-mercaptoalkyl phosphates[105]. Derivatives of acyclic and six- and seven-membered cyclic acids do not isomerise under these conditions.

An increase of the coordination number of the phosphorus atom has been observed in the dimerisation of 2-imino-2-R-1,3,2-diheterophospholans and their 4,5-benzo-analogues[97,106] to 1,3-diaza-2,4-diphosphetidines:



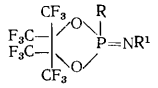
R = CH_2CH_2, *ortho*-C_6H_4 .

This process probably proceeds via a [2+2]-cycloaddition mechanism, but the dimerisation of the cyclic five-membered phosphorimidates obeys all the rules governing the nucleophilic substitution at the phosphorus atom. The presence of acyl groups at the nitrogen atom determines the stability of the monomeric form. If there is an aryl substituent at the nitrogen atom, then the capacity for dimerisation is determined by the nature of the substituents R^2: the dimethyl-amino-group attached to the phosphorus atom stabilises the monomer; weak electron-donating or electron-accepting groups at the phosphorus atom promote dimerisation. Acyclic phosphazo-compounds with the same environment around the phosphorus atom are monomeric[97].

A similar behaviour has been observed also in the series of 2-imino-4,5-benzo-1,3,2-dioxaphospholans[107,108]: regardless of the nature of the substituents at the phosphorus atom, the *N*-acyl derivatives are monomeric, while the *N*-aryl derivatives are dimeric. 2-Diethylamino-2-*N*-phenylimino-4,5-benzo-1,3,2-dioxaphospholan, which is involved in a monomer–dimer equilibrium in solutions, is an exception.

Evidently, the relative ease of the dimerisation of the five-membered cyclic phosphazo-compounds is ensured by the ring strain, which diminishes when the ring passes to the *a–e* position in the dimeric 1,3-diaza-2,4-diphosphetidine[106]. The greater tendency towards dimerisation by 4,5-benzo-derivatives can be accounted for by the greater strain in the condensed ring.

On the other hand, in the series of iminophospholan derivatives of perfluoropinacone (LXXVIII) the competing influence of the five-membered ring in the substituent at the phosphorus atom is manifested. Despite the presence of a bulky substituent in the imine fragment, which hinders dimerisation, compounds (LXXVIII) exist in the form of dimers, while the iminophospholan (LXXIX) is monomeric[109,110]:



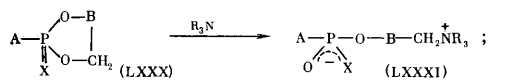
(LXXVIII), R=F; R^1 = t-C_4H_9, $Si(CH_3)_3$;
(LXXIX), R=N [$Si(CH_3)_3]_2$; R^1=$Si(CH_3)_3$.

The imino-derivatives of the 1,3,2-oxazaphospholan[97] and 1,3,2-dioxaphosphorinane[111] types are monomeric. In the latter case this is probably associated with the absence of ring strain in the six-membered ring.

III. NUCLEOPHILIC SUBSTITUTION AT A CARBON ATOM

Apart from the tetracoordinate phosphorus atom or together with the latter, a ring carbon atom or a carbon atom in an exocyclic ester group can serve as a centre of nucleophilic attack. The site of nucleophilic substitution is determined by the nature of the nucleophile and of the substituents at the ring carbon atoms and the carbon atoms of the exocyclic group.

The interaction of tertiary amines with 2-oxo-2-thiono-, and 2-selenono-1,3,2-dioxaphospholans and the corresponding phosphorinanes (LXXX) leads mainly to the formation of the inner salts (LXXXI):[112]



(LXXX) (LXXXI)

X=O, S, Se; A=R, RO, Ar, ArO, R_2N; B=CH_2, $(CH_2)_2$, *ortho*-C_6H_4 .

The rate of reaction is greatly influenced by the electronic properties of the exocyclic substituents. Under the usual conditions, the reaction terminates after several days for A = C_6H_5O and *p*-$NO_2C_6H_4O$ and after several months for A = R_2N.[113]

The ease of formation of the inner salts depends on the degree of ring substitution and the nature of the amine. In the series of 2-oxo-2-phenoxy-1,3,2-dioxaphospholans[114] salts of type (LXXXI) are formed only in the case of unsubstituted rings. Monomethylphospholan does not form inner salts in the reactions with methylamine and dimethylamine; attack is mainly directed to the phosphorus atom. Nucleophilic substitution at a ring carbon atom is even less marked for rings with a large number of methyl groups. In these reactions with amines one can postulate an S_N2 mechanism, which leads to ring opening and the formation of aminoalcohol derivatives (LXXXI): the reaction with the strong bases $(CH_3)_2NH$ and $(C_2H_5)_2NH$ is faster, whereas that with bases of moderate strength, namely pyridine and aniline, is slower. This mechanism apparently operates also in the reactions of unsubstituted rings. However, the fact that in the reaction of monomethylphospholan the nitrogen atom is linked to the methylated carbon atom suggests that the S_N1 mechanism is preferred[114].

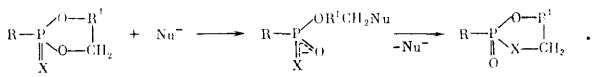
Exocyclic dealkylation by amines has been observed in 1,3,2-dioxaphospholan with alkoxy-substituents at the phosphorus atom[112,113]. Contrary to expectation, cyclic ammonium phosphates are formed also in the interaction of tertiary amines and pyridine with 4,5-dimethyl-2-oxo-2-phenoxy-1,3,2-dioxaphospholans and in the reaction of all the amines investigated with the phenyl ester of pinacone phosphate[114]. It has been suggested that in this case the amine attacks the phosphorus atom and the formation of phenylammonium cyclic phosphate is a result of a secondary disproportionation process arising in the first, phosphorane stage. Exocyclic dearylation also occurs when 5-chloromethyl-5-methyl-2-*p*-nitrophenoxy-2-oxo-1,3,2-dioxaphosphorinane reacts with sodium *p*-nitrophenoxide[115].

Thus an unsubstituted five-membered phosphate is attacked by amines at an endocyclic carbon atom. When the ring contains at least one methyl substituent, the reaction centre becomes either the carbon atom linked to the substituent or the phosphorus atom. A highly basic group attacks only the phosphorus atom; when the basicity is lower, there is competition between two electrophilic centres; interaction via the phosphorus atom can lead either to ring opening (in the case of strong bases) or to intramolecular disproportionation to ammonium phosphate[114]. The opening

of the phospholan ring under the influence of amines made it possible to develop a convenient method of synthesis of phosphorylcholines[116,117].

The endocyclic carbon atoms can undergo nucleophilic attack also by other nucleophiles, for example, by cyanide ions, with formation of 2-cyanoalkyl esters of phosphorus acid[118]. The substitution of the cyclic glycerol phosphates by phosphate anions has been used to synthesise glycerol phospholipids[119].

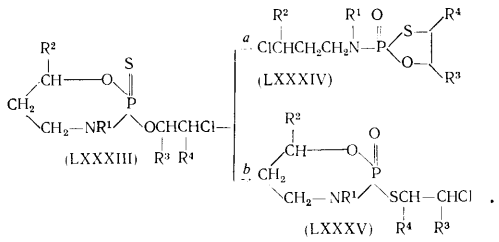
Nucleophilic substitution at a carbon atom in 2-selenono- and 2-thiono-2-R-1,3,2-dioxaphospholans and the corresponding phosphorinanes leads to selenone–selenol and thione–thiol isomerisation. The reaction proceeds via a stage involving the formation of the acyclic anions (LXXXII):



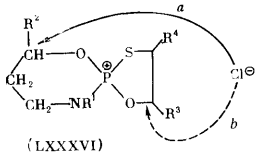
(LXXXII)

The isomerisation can take place under the influence of tertiary amines[113], tertiary phosphines[113,120], and iodide[121] and bromide[50] anions.

An interesting case of thermal thione–thiol isomerisation has been observed in the series of oxazaphosphorinanes with an exocyclic 2-chloroalkoxy-group (LXXXIII):



The reaction proceeds via two pathways (*a* and *b*) and leads to the products (LXXXIV) and (LXXXV), probably via the common intermediate (LXXXVI), which arises as a result of the intramolecular alkylation of the thiophosphoryl group:

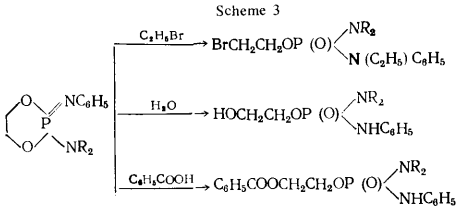


(LXXXVI)

In those cases where $R^2 = CH_3$ and $R^3 = R^4 = H$, the attack by the chloride anion proceeds via pathway *b* and the isomer with the oxazaphosphorinane structure (LXXXV) predominates in the mixture of products. On the other hand, the introduction of the methyl substituent into the chloroethyl group favours pathway *a*, which leads to the opening of the six-membered ring and to an increase of the content of the oxathiaphospholan (LXXXIV).[122]

Nucleophilic substitution at a ring carbon atom in 2-alkylamino-2-phenylimino-1,3,2-dioxaphospholans is accompanied by the imide–amide rearrangement[97,106] in accordance with Scheme 3:

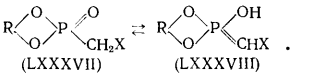
Scheme 3



Cyclic phosphorimidates are then more reactive than the acyclic derivative[97].

IV. COMPOUNDS WITH AN ACTIVE METHYLENE GROUP

Although the reactiviity of cyclic phosphonates with an active methylene group has been little studied[123], the available data indicate their unusual properties which are manifested both in their structures and in the characteristics of their reactions. Infrared spectroscopic and NMR studies on the phosphonates (LXXXVII) with $R = CH(CH_3)CH(CH_3)$ and $X = CN$ or $COOC_2H_5$ led to the discovery of the phosphonate–ylide tautomerism in the series of five-membered cyclic derivatives[124]:



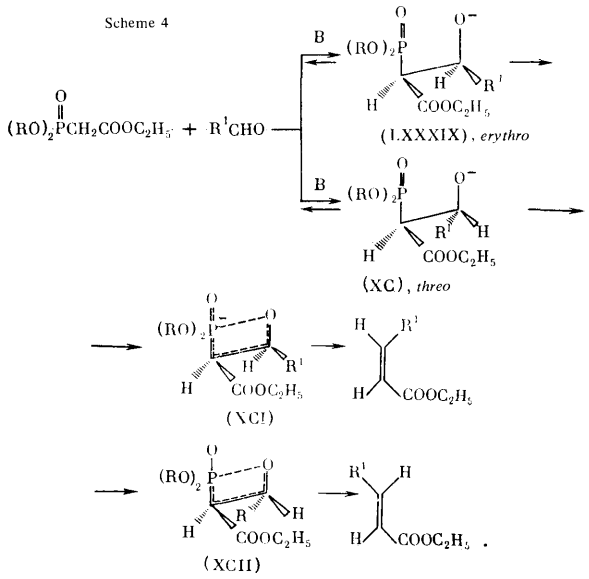
(LXXXVII) (LXXXVIII)

The ylide structure (LXXXVIII) was detected from the characteristic absorption of the OH group in the infrared region (3420–3460 cm^{-1}); the isomer ratio is 4 : 1 in favour of compound (LXXXVII) according to ^1H NMR data[124]. These compounds are titrated like strong monobasic acids and vigorously interact with diazoalkanes. The presence of the ylide formed is associated with the pronounced electron-accepting effect of the dioxaphospholan fragment (see Section V). The acyclic and six-membered cyclic esters and nitriles of phosphonoacetic acid are not converted into ylides and do not exhibit acid properties[124].

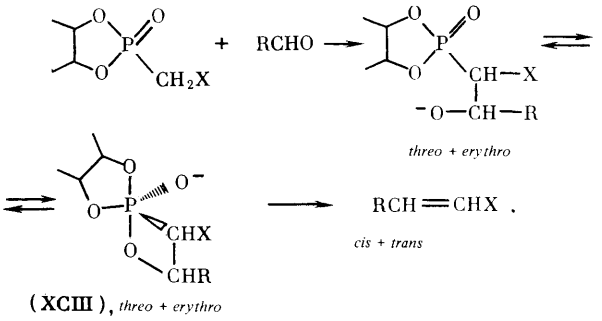
The incorporation of a phosphorus atom in the five- or six-membered rings of compounds (LXXXVII) alters appreciably the stereospecificity of the phosphonate modification of the Wittig reaction[125,126]. The reactions of acyclic organophosphorus compounds having an active methylene group with carbonyl compounds proceed preferentially with formation of *trans*-olefins[125–128]. This is attributed to the thermodynamic control of the reversible formation and interconversion of the *erythro*- and *threo*-betaines (LXXXIX) and (XC) and their decomposition to olefins.

In acyclic systems the stability of the intermediate monocyclic phosphoranes of type (XCI) and (XCII, R = alkyl) is apparently insufficient to prevent the epimerisation of the phosphonates (LXXXIX) and (XC) preceding them (Scheme 4):[126,127]

Scheme 4



The alkoxides (LXXXIX) and (XC) obtained from five-membered cyclic phosphonates (LXXXVII), rapidly form the more stable spirophosphoranes (XCIII), which should prevent the interconversion of the *erythro*- and *threo*-intermediates and hence should favour the formation of appreciable amounts of *cis*-olefins (the ratio of *cis*- and *trans*-olefins in reactions of five-membered cyclic phosphonates is close to 60:40 [126]). The study of ^{31}P NMR spectra of the reaction mixture of compound (LXXXVII), where R = $CH(CH_3)CH(CH_3)$ and X = $COOC_2H_5$, with benzophenone and aryl cyclopropyl ketones made it possible to demonstrate the formation of a spirophosphetan of type (XCIII):[129]



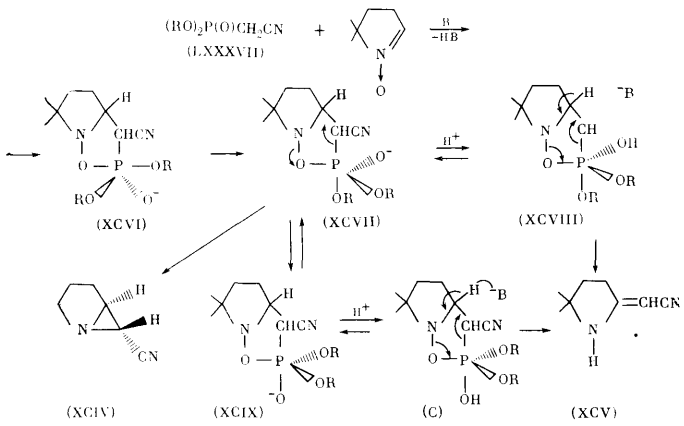
(XCIII), *threo + erythro*

Phosphonates of the dioxaphosphorinane series also produce considerable amounts of *cis*-olefins in these reactions[128], but their content is appreciably lower, which may be attributed to the lower stability of the intermediate phosphoranes with a six-membered ring than that of the compounds with a five-membered ring (the effect of the five-membered ring).

The size of the phosphorus-containing ring in phosphonates with an active methylene group influences also the reactions with nitrones. The interaction of acyclic phosphonates with nitrones in aprotic solvents leads to the preferential or exclusive formation of the aziridines (XCIV), while in protic solvents this reaction proceeds to the enamines (XCV) whose content increases with the acidity of the medium[130–132]. These results have been interpreted on the hypothesis that the intermediate (XCVI) participates in the process. The formation of the reaction product requires the transfer of a carbon atom in compound (XCVII) to the *a*-position via permutation isomerisation; the decomposition of compound (XCVIII) leads to the formation of an aziridine. Protonation neutralises compound (XCVII) and 1,2-elimination from compound (XCVIII) gives rise to the enamine (XCV).

The reaction of the five-membered phosphonate (LXXXVII), where R,R = $CH(CH_3)CH(CH_3)$, proceeds via the intermediates (XCVII) and (XCVIII), whose stabilisation is improved by virtue of the *a–e* disposition of the two five-membered rings. The decomposition of compound (XCVII) also leads to a single product of the reaction of 2-cyanomethyl-3,4-dimethyl-2-oxo-1,3,2-dioxaphospholan, namely the aziridine (XCIV).[133] In the six-membered 5,5-dimethyl-1,3,2-dioxaphosphorinane derivative (LXXXVII), where R,R = $CH_2C(CH_3)_2CH_2$, the *a–e* position of the six-membered ring in the boat conformation[61,62] gives rise to the unfavourable non-bonding 1,4-interaction of the *gem*-dimethyl groups with the substituent at the phosphorus atom. For this reason, the intermediate (XCIX) with an *e–e* ring in the chair conformation, where the oxide anion occupies the *a*-position, is preferable. It is known that the oxide anion in the *a*-position is a stronger base[13] and is rapidly protonated to compound (C) with subsequent β-elimination of an enamine. Under these conditions, the weaker base (XCVII) remains in the form of an anion (in the reactions of the five-membered phosphonate) and decomposes to aziridine (Scheme 5).

Scheme 5



In the reactions of the phosphonate (LXXXVII), where R,R = $CH(CH_3)CH(CH_3)$ and X = CN, the formation of a spirophosphorane, which gives rise to high-field signals (−35 and −36 p.p.m.) in ^{31}P NMR spectra, was demonstrated[134].

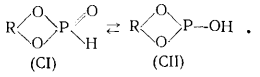
V. CYCLIC PHOSPHORUS ACIDS

1. Alkylenephosphorous Acids

The principal data on the methods of synthesis, stereochemical features, and certain reactions of alkylenephosphorous acids are presented in a recently published review[135]. We shall therefore consider below only the result of later studies and those which permit inferences about the chemical consequences of the incorporation of the hydrophosphoryl fragment in a five- or six-membered ring.

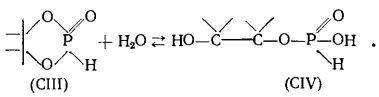
As in cyclic six-membered phosphates, among 1,3-alkylene phosphites, the stereoisomer with the P=O group in the *e*-position is more stable. Whereas in six-membered hydrophosphoryl compounds the conversion of the labile forms into stable forms takes place fairly readily, the analogous 1,3,2-dioxaphospholans do not tend to undergo the conversion readily[135].

The acid-base properties of alkylene phosphites and the influence of dihydroxyalkylene substituents on the diad tautomerism have been investigated:



The study of alkylenephosphorous acids in alcoholic[136] and aqueous alcoholic media[137] demonstrated the anomalously high acidity of the five-membered hydrophosphoryl compounds, which was explained by the presence of considerable amounts of the phosphite form (CII) and by the electron-accepting influence of the 1,2-dihydroxyalkylene groups. However, a detailed study of the acid–base properties of methyl pinacolphosphorous acid in aqueous organic solvents[138–140] made it possible to relate its high acidity to its ready

reversible hydrolysis to the monoalkyl phosphite (CIV), which is responsible for the highly acidic properties of the methyl pinacol phosphite:



(CIII) (CIV)

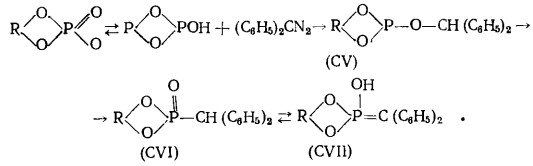
On the other hand, the reversibility of the hydrolysis of 2,3-butylene phosphite was not observed[139]; unusual ease of recyclisation is specific solely to the methyl pinacol phosphite derivative (the Ingold–Thorpe effect). A considerably smaller acidity has been found for 4,5-dimethyl-2-oxo-2-phenyl-1,3,2-dioxaphospholan[137]. Factors other than the contribution of structure (CIV) (for example, the CH acidity of the ring) probably play a role in this instance. The considerably smaller strength of methyl pinacol phosphorothious acid compared with the oxo-analogue is also striking (the pK_a in 50% ethanol are 4.76 and 2.37 respectively[141]); this difference is difficult to account for from the standpoint of hydrolysis, because the thiono-analogue of the acid (CIV) should be more acid or at least comparable in its acidity.

Possibly the protonated forms of compounds (CI) and (CII) contribute to the overall acidity of cyclic hydrophosphoryl compounds[137,141] and their formation is characteristic mainly of five-membered cyclic derivatives. The six-membered and acyclic hydrophosphoryl compounds have similar acid properties[137,139,141].

The contribution of the phosphite form to the equilibrium (CI) ⇌ (CII) involving five-membered alkylene phosphites is apparently less important than for the six-membered and acyclic derivatives[137]. In ethylene phosphoromonothiolite the content of form (CII) is estimated as ~30%;[142] catecholphosphorous acid exists in the condensed phase mainly in the phosphorus (III) form and both isomers are detected only in solutions[137].

The more marked tendency of five-membered alkylene phosphites to isomerise to the phorphorus(III) derivatives has been used to explain the characteristics of the chemical behaviour of these hydrophosphoryl compounds. Thus cyclic phosphorous and phosphorothious acids of the 1,3,2-dioxaphospholan series readily combine with sulphur in the absence of catalysts with formation of alkylenephosphoro-monothious and alkylenephosphorodithious acids[141]. Six-membered phosphorothioites combine with sulphur in the presence of bases[143]; this reaction is not characteristic of acyclic hydrothionophosphoryl compounds[144].

Fundamental differences between the reactivities of acyclic and cyclic hydrophosphoryl compounds have been noted for their reactions with diphenyldiazomethane. Whereas the former react with diazoalkanes only under severe conditions with formation of phosphorus–nitrogen derivatives[145,146], cyclic phosphates interact vigorously with diazo-derivatives, the reaction being accompanied by a rise of temperature and the evolution of nitrogen even in the cold[147]. The reaction proceeds via a stage involving the formation of diphenylmethyl phosphite (CV), which subsequently isomerises to the phosphonate (CVI) in equilibrium with the ylide (CVII):



(CV) (CVI) (CVII)

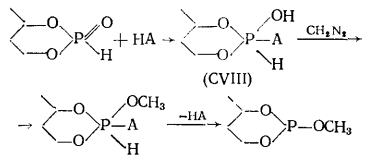
Kinetic studies of the two-stage formation of compound (CV) demonstrated the similarity of the mechanisms of the reactions of cyclic phosphites[148] and acids based on phosphorus in the highest oxidation state[149], which include the initial proton transfer and subsequent decomposition of the resulting ion pair:

$$HA + (C_6H_5)_2CN_2 \xrightarrow{k_1} HN_2C(C_6H_5)_2^+A^- \xrightarrow{k_2} \text{product.}$$

It was established that five-membered alkylene phosphites react faster by a factor of 3–12 than the six-membered derivatives and diphenyl phosphite, in conformity with the strengths of these acids. Measurement of the rate of consumption of the diazo-component and of the accumulation of nitrogen made it possible to compare the rates of the two stages. It was found that the rates of reaction measured by the two methods and the activation parameters are similar for the least reactive neopentyl- and diphenyl-phosphorous acids, i.e. $k_1 > k_2$. For the more acid 2,3-butylene phosphite, the rate of evolution of nitrogen is smaller by an order of magnitude than the rate of consumption of the diazo-compound[148]; in this case the slow stage of the process is the unimolecular decomposition of the ion pair ($k_2 > k_1$).

The intermediate formation of the diphenylmethyl phosphite (CV) has been demonstrated in the reaction of catechol phosphorous acid[147] and the capacity for the subsequent transformation into a phosphonate and an ylide was demonstrated in a study of compound (CV), obtained by the reaction of 2,3-butylene phosphorochloridite with diphenylmethanol.

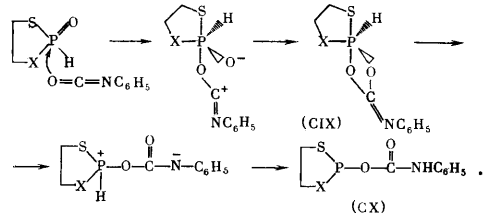
We may note that the interaction of 1,3-butylene phosphite with diazomethane in protic media has been attributed to the involvement of the phosphorane adduct (CVIII):[150]



(CVIII)

However, this mechanism does not explain the non-catalysed reaction of alkylene-phosphorous acids and phosphorothioites in aprotic media[148].

The addition of five-membered alkylenephosphorous acids to unsaturated systems also proceeds with a decrease of the coordination number of the phosphorus atom. Thus phenyl isocyanate combines with ethylene phosphoromono-thioites and phosphorodithioites with formation of the phosphorus(III) derivatives (CX),[142] probably via a mechanism involving the nucleophilic addition of the acid to the tautomeric form with a tervalent phosphorus atom or the addition of their conjugate alkylene phosphite anions to the C=N bond of phenyl isocyanate. An alternative mechanism presupposes nucleophilic attack by the carbonyl oxygen atom of the unsaturated reactant on the tetrahedral phosphorus atom in the alkylene phosphite[135]. This course of the reaction involves the formation of the intermediate (CIX) with a high energy, which is due to the considerable angular strain in the dioxaphosphetan ring incorporating an sp^2-hybridised carbon atom:



(CIX) (CX)

Adducts with a phosphite structure are formed as a result of the non-catalysed addition of catechol phosphorous acid to styrene, anethole, and butyl vinyl ether[151]. Phosphites isomerise more or less readily to phosphonates. Intermediates with phosphorus(III) could not be detected in the reactions of 2,3-butylene phosphite and phosphorothioite with butyl vinyl ether. It is noteworthy that acyclic phosphorous acids do not undergo heterolytic addition to compounds whose double bond is nucleophilic[152,153].

2. Quinquevalent Phosphorus Acids. The Electronic Influence of Dihydroxyalkylene Substituents

In contrast to the types of organophosphorus compounds examined above in which the reactive centre is mainly the phosphorus atom, the reaction of phosphorus(V) acids  , where R = 1,2- or 1,3-alkylene and X,Y = O or S, are characterised by the involvement of the functional groups in the side chain, while the phosphorus-containing cyclic substituents exert a specific influence on them.

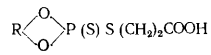
Cyclic phosphonic and phosphinic acids have on the whole acidities comparable to those of the acyclic phosphonates and phosphinates[154-159], although the strain in the five- and four-membered rings[154,155] leads to some enhancement of the acid properties.

However, a number of acids of the 1,3,2-dioxaphospholan and 1,3,2-dioxaphosphorinane series were found to exhibit appreciable differences from the phosphinate derivatives in aqueous alcoholic media in which potentiometric studies were carried out[158].

Comparison of the pK_a of substituted six-membered phosphoric acids in aqueous ethanol solutions, absolute ethanol, and nitromethane permitted the hypothesis[156,157,159] that there is a possibility of the specific solvation of the dihydroxyalkylene substituents at the phosphorus atom in aqueous organic media. Calorimetric and spectroscopic studies[160] of the solvation of isotypical cyclic and acyclic phosphorus and carbon compounds led to the discovery of a difference between the types of solvation of the cyclic compounds, on the one hand, and the acyclic compounds, on the other; no anomaly was found in water–alcohol mixtures. Nevertheless the available data are still insufficient to infer the nature of this difference.

Cyclic phosphoromonothioic acids[161] are stronger in aqueous alcoholic media than their acyclic analogues[162], which may be due to a more significant contribution to the tautomeric thione–thiol equilibrium by the thiolo-form of cyclic phosphorothioates[161]. This hypothesis is consistent with the results of the determination of the oxidation-reduction potentials of the latter compounds in these solutions[163]. In solvents with a lower polarity the thiono-forms of cyclic phosphoromonothioic acids predominate[136].

Cyclic phosphorodithioic acids also exhibit stronger proton-donating properties in benzene and anisole than the acyclic acids[164]. However, in absolute ethanol the values of pK_a of alkylene phosphorodithioates are higher than for their analogues with an open-chain structure. This anomaly of the acid properties was explained by the conformational characteristics of these cyclic compounds. Thus the *cis*-disposition of the exocyclic S–H and P–S groups in dioxaphospholan derivatives makes the proton less mobile and the effective positive charge on the phosporus is "quenched" as a result of the solvation by ethanol molecules which are of suitable size[165]. Such *cis*-orientation in the triad P(S)SH predetermines the possibility of the formation of intramolecular hydrogen bonds in the molecules of five-membered cyclic phosphorodithioates[166].

The removal of the acid centre from the phosphorodithioate substituent in acids of the type 

promotes a change in the mutual orientation of the functional groups and the manifestation of a greater electron-accepting capacity by 1,2-dihydroxyalkylene substituents compared with the alkoxy-substituents[167].

The study of the acid–base properties of the acids of phosphorus in the highest oxidation state is important for the determination of the electronic influence (σ^{ph}) of dihydroxyalkylene substituents at the phosphorus atom. However, the use of the ionisation constants of oxygen-based cyclic phosphates for the calculation of the σpH on the basis of Kabachnik's familiar standard series[168] proved to be impossible, because it was shown[156,157] that cyclic and acyclic phosphates are acids of different chemical types. Because of this, the values of σ^{ph} determined from this series do not exhibit the required constancy—they vary as the solvent is altered (Table 2, Nos.12–15).

Attempts have been made to determine the values of σ^{ph} of dihydroxyalkylene substituents from other reaction series: from the free energies of the association of cyclic phosphoryl compounds with *p*-fluorophenol[169], the basicity constants, ^{19}F NMR data for phosphorimidate compounds[170], and the stability constants of phosphinodithioyl complexes of cobalt[172]. Analysis of the results (Table 2) showed that invariant values of the σ^{ph} constants can be assigned only to alkylene (Nos.1 and 10) and dihydroxytetramethylene (No.20) substituents. For other 1,2- and 1,3-substituents, this is at present difficult to achieve.

One of the causes of the inadequately clear-cut quantitative ideas concerning the influence of these types of substituents at the phosphorus atom is the lack of exact views on the nature of the solvation and transolvation of the cyclic fragment containing a phosphorus atom. Admittedly, this factor cannot be decisive because the values of σ^{ph} for acyclic groups are fairly satisfactory in different reaction series and in media of different polarity[173].

One must also note the dependence of the σ^{ph} of the groups RX not only on the nature of the inductive and resonance components in the overall polar effect of substituents[173] but also on their steric influence[174-177]. This is apparently equally valid also as regards the groups X–R–Y at the phosphorus atom, although one cannot rule out the possibility that in the case of cyclic substituents hyperconjugation and field influences can be manifested together with the effects enumerated above.

On the other hand, there are data showing that the steric effect of dihydroxyalkylene substituents with sterically fixed configurations is less pronounced than the effect of two alkoxy-groups having the same number of carbon atoms[178].

Thus a realistic estimation of the relative contributions of the inductive, mesomeric, and structural components to the overall values of σ^{ph} for cyclic substituents at the phosphorus atom is at present fairly difficult. Only certain qualitative conclusions can be drawn from the available data (Table 2): the strained phospholan substituents have the most marked electron-accepting properties; the influence of the phosphorinane fragments is similar to the overall effect of two acyclic alkoxy-groups at the phosphorus atom.

It has been suggested that the enhancement of the electron-accepting effect of the 1,2-dihydroxyalkylene substituent at the phosphorus atom in a five-membered ring

Table 2. The values of σ^{ph} for cyclic substituents at the phosphorus atom.

№	Substituent A + B	From the pK_a for the acids ABPOOH					α	β	γ	References
		H_2O	50% C_2H_5OH	80% C_2H_5OH	95% C_2H_5OH	CH_3NO_2				
1	$-(CH_2)_4-$	−1.84	−1.62	−1.83*	−1.71	−1.77	−1.78	—	—	[157, 169]
2	$-O(CH_2)_3-$	—	—	—	—	—	−1.01	—	—	[169]
3	$-O(CH_2)_2N(CH_3)-$	—	—	—	—	−1.19**	—	−0.30	—	[170]
4	$-O(CH_2)_2N(C_6H_5)-$	—	—	—	—	−0.13**	—	+0.93	—	[170]
5	$-O(CH_2)_2N$ (iso-C_3H_7)—	—	—	—	—	—	−1.17	—	—	[169]
6	$-O(CH_2)_2O-$	—	—	—	—	—	+0.11	+0.90	—	[169, 170]
7	$-OCH(CH_3)CH_2O-$	—	—	—	—	—	−0.02	+0.75	+1.21	[139, 164, 170]
8	$-OCH(CH_3)CH(CH_3)O-$	—	—	—	—	—	—	—	+0.62	[164]
9	$-OC(CH_3)_2C(CH_3)_2O-$	—	—	—	—	—	−0.05	—	+0.10	[164, 169]
10	$-(CH_2)_5-$	−2.18	−1.95	−2.12	−1.97	−2.27	−2.26	—	—	[157, 169]
11	$-O(CH_2)_4-$	—	—	—	—	—	−1.44	—	—	[169]
12	$-O(CH_2)_3O-$	−0.87	−0.64	−0.25	−0.08	−0.14***	−0.56	+0.02	—	[157, 169]
13	$-OCH(CH_3)CH_2CH_2O-$	−0.75	−0.65	−0.42	−0.27	−0.20	−0.55	—	+1.06	[157, 169, 171]
14	$-OCH(C_6H_5)CH_2CH_2O-$	−0.67	−0.54	−0.18	+0.06	+0.01	−0.47	—	—	[157]
15	$-OCH_2C(CH_3)_2CH_2O-$	−0.67	−0.57	−0.19	0.00	−0.08	−0.46	—	+1.73	[157, 164, 169]
16	$-OCH$ (iso-C_3H_7)$C(CH_3)_2CH_2O-$	—	—	—	—	—	−0.54	—	—	[139]
17	$-O(CH_2)_3N$(iso-C_3H_7)-	—	—	—	—	—	−1.72	—	—	[169]
18	$-CH_2SCH_2$	+0.195	—	—	—	—	—	—	—	[155]
19	$-N(t\text{-}C_4H_9)CH=C(t\text{-}C_4H_9)O-$	—	—	—	—	—	+0.5****	—	—	[172]
20	$-O(CH_2)_4O-$	−0.58	−0.66	−0.60	−0.39	−0.49	−0.72	—	—	[139]
21	$-O(CH_2)_2N$(iso-C_4H_9)-	—	—	—	—	—	−1.24	—	—	[139]

Note. α, β, and γ are the values of σ^{ph} found from the thermodynamic characteristics of the hydrogen-bonded complexes of cyclic phosphoryl compounds with *p*-fluorophenol, the chemical shift $\delta(^{19}F)$ of fluorine-substituted arylimides of cyclic phosphorus acids, and the stability constants of the cobalt complexes of phosphorus dithioacids respectively.

*The value of σ^{pH} found from the pK_a for the acids ABPSOH is −1.65.[161]

**Found from the basicity constants of the arylimides of cyclic phosphorus acids.

***The value of σ^{ph} found from the basicity constants of the arylimides of cyclic phosphorus acids is −0.61.[170]

****Found from the correlation between the values of σ and the stretching vibration frequencies of the phosphoryl groups ν(P–O) in the compounds ABP(O)R.

is associated with the rigid fixation of the oxygen atoms, which weakens the p_π–d_π interaction of the unshared electron pairs of the endocyclic oxygen atoms with the *d* orbitals of phosphorus[179]. This increases the electron density deficit at the tetracoordinate phosphorus atom and reduces the basicity and nucleophilicity of the trivalent phosphorus atom in a 1,3,2-dioxaphospholan ring. We may note that the more pronounced electron-accepting properties of the 1,2-dihydroxyalkylene group compared with two alkoxy-groups are also attributed to the decrease of the endocyclic P–O–C angles, which alters the hybridisation of the oxygen atom from sp^2 towards sp^3, and to a decrease of the π character of the ring P–O ester linkages[180].

The reactivity of phosphorus(V) acids has been studied more extensively in relation to phosphorus dithio-acids. In the general case, cyclic phosphorodithioates are more reactive than their acyclic analogues. Thus their reaction with diphenyldiazomethane is accompanied by a greater heat change[181], they add faster to acrylonitrile[182], and they are more reactive in the protodemetallation reaction of tetra-ethylstannane[184]. This is mainly associated with the greater strength of the cyclic dithio-acids compared with the acyclic analogues.

On the other hand, the complexes of transition metal ions nickel(II), cobalt(II), silver(II), and zinc(II) with cyclic phosphinodithioyl ligands are less stable than the complexes with dialkoxyphosphinyl ligands[172,185,186], which can be naturally accounted for by the greater electron-accepting capacity of the cyclic ligands. For the same reason, the alkylation of salts of cyclic dithio-acids[183] is much slower than that of the acyclic acids[187].

The kinetics of the addition of cyclic phosphorodithioates to α-substituted styrylphosphonates and ethyl acrylate are unusual[188,189]. Whereas acyclic phosphorodithioates interact with these unsaturated reagents via the bimolecular nucleophilic addition mechanism with 1,4-orientation of the dithio-acid with respect to the system of multiple bonds of the unsaturated reactant, in the case of the stronger cyclic dithio-acids the rate of reaction is described by a third-order equation: of first order with respect to the unsaturated reactant and of second order with respect to the acid. In the first stage a hydrogen-bonded complex of the dithio-acid with a protophilic centre of the unsaturated compound (P=O or C=O) is formed and then a second molecule of the cyclic phosphorodithioate adds to the multiple bond.

* * *

The data presented in this review demonstrate the wide variety of the reactivities of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes, expressed both in the anomalous rates of reaction and in the unusual pathways followed in the interactions, which are not characteristic of their acyclic analogues. The fairly considerable ease of the change in the coordination number of the phosphorus atom, $P^{IV} \rightleftharpoons P^{V}$–$P^{VI}$, due to the favourable thermodynamic features of the trigonal and tetragonal bipyramids of penta-coordinate and hexacoordinate phosphorus compounds containing five-membered heterocycles, has been demonstrated in relation to cyclic and particularly five-membered organophosphorus compounds. The study of the reactivity

of cyclic derivatives of phosphorus acids established the important role in chemical reactions of intermediates containing phosphorus atoms in the highest coordination states. This made it possible in its turn to consider the fine details of many biochemical processes occurring with participation of phosphate esters. On the other hand, the available information about the interconversion of phosphorus compounds with different coordination numbers revealed and explained the unity and wide variety of the chemistry of organophosphorus compounds.

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The Strain Energy, Geometrical Structure, and Spin-Spin Coupling Constants of Cyclic Hydrocarbons

M.P.Kozina, V.S.Mastryukov, and E.M.Mil'vitskaya

The thermochemical data and spin-spin coupling constants (SSCC) are compared with the geometrical parameters of molecules investigated in the gas phase by electron diffraction and microwave spectroscopy. Cycloalkanes C_nH_{2n}, cycloalkenes C_nH_{2n-2}, cyclo-1,3-dienes, bicyclo[n.1.0]alkanes, and bicyclo[$n.m$.1]alkanes have been chosen as objects of investigation. Using the method of least squares, 13 empirical equations, relating the strain energy and the SSCC, on the one hand, to the internuclear distances and the valence and dihedral angles, on the other, have been fitted. The equations can be used to estimate the characteristics of compounds which have not been investigated.
The bibliography includes 170 references.

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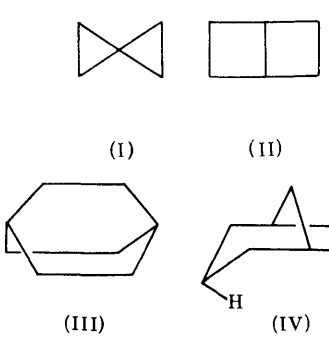
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I. INTRODUCTION

Two features are characteristic of the concept of strain, which is widely used in organic chemistry. On the one hand, the fundamental postulates of the concept are intuitively understood and permit easy qualitative predictions; on the other hand, quantitative estimates are difficult and are of a conventional kind, because the concept of "strain" has no rigorous definition[1].

It has come to be assumed that the molecule has a certain excess energy if its geometrical parameters differ from those characteristic of the "unstrained" system, adopted by convention as the starting point for calculations, the reference system, or standard. In order to discover individual types of strain in the molecule, it is sometimes sufficient to inspect its structural formula. In other cases it is necessary to construct three-dimensional models or to carry out special calculations. We shall describe as an example several molecules whose geometry is known.

For example, angular strain can be specially readily deduced in the spiropentane (I).[2] The deformations of the internuclear distances are less evident, but it can be assumed that the common bond in bicyclo[2.2.0]hexane (II) [3] must be extended if it is supposed that the molecule is formed from cyclohexane by the insertion of a bond between the 1- and 4-positions. Bicyclo[2.2.2]octane (III) may serve as an example of a molecule with a dominant torsional strain (the presence of eclipsed conformations).[4] Finally, repulsive van der Waals interactions between non-bonded hydrogen atoms have an appreciable influence on the conformation of a molecule such as that of bicyclo[3.3.1]nonane (IV).[5]



(I) (II) (III) (IV)

Thermochemical data constitute the experimental basis for the quantitative estimation of the strain energy E_S. Information about the geometrical structure of the molecules has been most frequently resorted to for their interpretation, although quantitative correlations have not been analysed[6-10]. On the other hand, an appreciable parallelism between the changes in E_S and molecular characteristics such as, for example, spectroscopic properties[11] and Compton profiles[12] has also been noted.

Comparison with the geometry is widely used also in the analysis of the spin–spin coupling constants (SSCC); the correspondence between the structure factors, the strain in the molecules, and the SSCC has been frequently pointed out in NMR studies.

For a number of reasons, cyclic hydrocarbons constitute the most promising objects for the search for a correlation between the above parameters:

$$E_s\text{-molecular geometry-SSCC.} \qquad (1)$$

Firstly, cyclisation of a hydrocarbon is as a rule accompanied by considerable changes in its geometry, which lead sometimes to the appearance of strain amounting to several tens of kcal mol^{-1}. Secondly, cyclic hydrocarbons are the most important structural units in organic chemistry, forming sequences of molecules with similar structures gradually increasing in complexity, which are being actively investigated by thermochemical and NMR methods. Accurate geometrical data obtained in the gas phase are available for many compounds. This is very important because only in the gas phase is the molecular geometry closest to the equilibrium geometry as a consequence of the absence of intermolecular interactions[13].

In the present review an attempt is made to compile and survey the experimental data published up to 1979 and characterising the strain energy, the geometrical structure, and the SSCC of cyclic hydrocarbons and to analyse the relation between these parameters using a minimum number of assumptions. It was found that the relations between the parameters can be analysed only in relation to cycloalkanes, cycloalkenes, cyclo-1,3-dienes, bicyclo[n.1.0]alkanes, and bicyclo[$n.m$.1]alkanes, which have been most thoroughly investigated on the lines indicated. We confined ourselves to the consideration of only unsubstituted hydrocarbons, since little information is available about substituted cycloalkanes and it is non-systematic. An exception has been

made for hydrocarbons of the cyclopropane series in order to survey the numerous thermochemical data which have been published in the last decade.

1. Calculation of the Strain Energies

The strain energy E_S of a cyclic compound is understood as the energy of the molecule in excess of that of the corresponding acyclic chain. The quantitative estimation of E_S presents considerable difficulties and is of a conventional kind[1,10,14]. The energies E_S can be estimated from the experimental enthalpies of combustion (ΔH_c°) or formation (ΔH_f°) and the enthalpies of hydrogenation (ΔH_h°) with the aid of additive computational schemes and by methods of calculation based on a mechanical model of the molecule and approximate quantum-chemical calculations.

Approximate quantum-chemical calculations of E_S are performed comparatively rarely and are of interest for an approximate estimation of ΔH_f°.[15] In calculations on complex molecules by this method, it is necessary to introduce many approximations, which leads to a considerable freedom in the selection of parameters and discrepancies between the results obtained by different workers[16].

Within the framework of the mechanical model of the molecule[9] (the term "molecular mechanics" is used in the foreign literature[17,18]), the energies E_S are calculated as sums of the individual contributions of the energies associated with the deformations of the bond lengths and angles (compared with ideal molecules), the torsional strain, and the interaction of atoms not linked by valence bonds. The method of molecular mechanics has been examined critically by Engler et al.[18] (see also other communications[19-21]).

The values of E_S obtained by comparing the experimental ΔH_f° with quantities calculated assuming additivity for hypothetical unstrained molecules with the same number and types of bonds are used in the present study. Hence it follows that the values of E_S depend both on the reliability of the experimental thermochemical data and on the selected method for their calculation for the chosen unstrained reference molecules, which are usually open-chain analogues (as in structural studies).

Not all compounds with an open chain of carbon atoms are free from strain. In branched acyclic molecules repulsive interactions inevitably arise between non-bonded atoms (mainly *gauche*-interactions). In estimating E_S one must therefore employ only computational schemes (based on the additivity of the bond energies or group contributions) in which the contribution of the *gauche*-interactions is isolated and highly branched acyclic molecules (for which interactions of another type are characteristic) are not considered. Table 1 presents the values of E_S for cyclo-alkanes obtained by computational schemes of this type[10,22-24].

It follows from Table 1 that there are discrepancies between the values of E_S even when isotypical computational schemes are used. For a comparison of the E_S, it is therefore desirable to employ the same computational scheme for all the compounds considered. In the present study the E_S were evaluated by an additive scheme[22] in which the group contributions were obtained not only for hydrocarbons but also for their derivatives, which extends its applicability. The strain energy is defined as the difference between the experimental and calculated enthalpies of formation ΔH_f°:

$$E_s = \Delta H_{f(G),e}^\circ - \Delta H_{f(G),c}^\circ \qquad (2)$$

where $\Delta H_{f(G),c}^\circ$ is equal to the sum of the group contributions.

Table 2 presents only those group contributions which we used to calculate the $\Delta H_{f(G)}^\circ$ for hypothetical unstrained molecules corresponding to the hydrocarbon considered.

Table 1. The strain energies of cycloalkanes (E_S, kcal mol^{-1}) at 298 K.

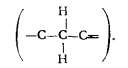
n	1 [22]	2 [10]	3 [23]	4 [24]	n	1 [22]	2 [10]	3 [23]	4 [24]
3	27.6	28.1	28.0	27.5	7	6.4	7.7	7.3	6.3
4	26.6	27.3	27.1	26.5	8	9.9	11.3	10.9	9.7
5	6.0	6.9	6.7	5.9	9	12.8	14.4	14.0	12.6
6	0.2	1.3	1.0	0.1	10	12.6	14.4	13.9	12.4

Notation: n is the number of carbon atoms in the ring and the numerals 1, 2, 3, and 4 denote computational schemes. Note. The numbers in square brackets in this and other Tables as well as in the formulae in the text denote references (Ed.of Translation).

Table 2. The group contributions to $\Delta H_{f(G)}^\circ$ (kcal mol^{-1}) at 298 K*.

Group	Contribution	Group	Contribution
$C-(C)_2(H)_2$	−4.95	$C-(C_d)_2(H)_2$	−4.29
$C-(C)_3(H)$	−1.90	$C_d-(C)(H)$	8.59
$C-(C)(C_d)(H)_2$	−4.76	$C_d-(C_d)(H)$	6.78

*The designations of the groups are the same as in the review of Benson et al.[22] For example, $C-(C)(C_d)(H)_2$ means that the group contains a saturated carbon atom C linked to one similar carbon atom (C), to one carbon atom involved in a double bond (C_d), and to two hydrogen atoms $(H)_2$, i.e. it represents the group



The extent to which E_S is arbitrary depends on the possibility of selecting an unstrained system (computational scheme), as mentioned above, and on the different influences (not taken into account when any computational scheme is employed) of (a) temperature, (b) zero-point energy (i.e. the energy of nuclear movement), and (c) the energy $p\Delta V$ on the $\Delta H_{f(G)}^\circ$ for the real cyclic molecule and the hypothetical molecule assumed to be unstrained.

It is necessary to estimate the limits within which the values of E_S can vary as a result of the influences of the three factors.

(a) The heat capacities of acyclic hydrocarbons can be assumed to be additive. For example, the contribution of the group $[C-(C)_2(H_2)_2]$, i.e. of $-CH_2-$, to C_p is 5.5 cal mol^{-1} K^{-1}.[11] The contribution of the $-CH_2-$ group obtained from the experimental C_p (25.40 cal mol^{-1} K^{-1}) for cyclohexane[22] is 4.2 cal mol^{-1} K^{-1}. Owing to the difference between the values of C_p per $-CH_2-$ group in the ring and in the hypothetical unstrained molecule, the value of E_S for a six-membered ring is too low by more than 2 kcal mol^{-1} at 298.15 K.

(b) The vibrational energy in n-alkanes can also be regarded as additive (on average, 17.50 kcal mol^{-1} corresponds to the $-CH_2-$ group[25-27]). A specific vibrational energy different from that of a hypothetical unstrained molecule is characteristic of each cyclic compound, but the difference should not be large, because the main contribution to the zero-point energy comes from the vibration frequencies of the C–H bonds, which are comparatively insensitive to molecular structure. For the majority of hydrocarbons considered, the zero-point energy cannot be calculated because the complete set of vibration frequencies is unknown. Quantitatively this can be illustrated in only a few examples: the vibrational energy for cyclohexane, calculated as $N\sum_i \frac{1}{2}h\nu_i$ (where N is the Avogadro number, h the Planck constant, and ν_i the frequencies of the fundamental vibrations) is 104.5 kcal mol^{-1},[26] while the value estimated from the group contributions (6×17.50) is 105.0 kcal mol^{-1}; the corresponding values for cyclopentane are 86.0 and 87.5 kcal mol^{-1} and those for cyclobutane are 67.3 and 70.0 kcal mol^{-1}. Consequently, according to these data, the value of E_S may be too high owing to failure to take into account the difference between the zero-point energies, for example, by 3 kcal mol^{-1} for cyclobutane. According to the results of another study[14], the energy E_S for cyclobutane is too high by 4.6 kcal mol^{-1} and the corresponding errors for three-, five-, and six-membered rings are 4.2, 3.7, and 3.4 kcal mol^{-1}.

Table 3. Changes in the strain energy (ΔE_S, kcal mol^{-1}) on passing from a three-membered to a six-membered ring obtained from different thermodynamic quantities*.

n	ΔE	ΔE_0	ΔE_{298}	ΔE_S
3–4	1.0	0.9	1.4	1.4
4–5	20.8	19.8	19.9	19.9
5–6	6.4	5.7	6.1	6.1

*Notation: ΔE are the differences between the strain energies obtained from the internal atomisation energies in the hypothetical equilibrium state at 0 K and 298 K; the ΔE_S were obtained from the enthalpies of atomisation at 298 K; n is the number of carbon atoms in the ring.

The mutually compensating influences of the thermal (a) and zero-point (b) energies result in the approximate constancy of the differences in the E_S on passing from one ring to another regardless of whether the thermal and zero-point energies are excluded or taken into account in the calculations. Table 3 presents the differences between the E_S for several cycloalkanes according to Nelander and Sunner[14]. Consequently, in order to compare the E_S for a specific series of compounds, one can also employ other available quantities, such as ΔH_f° (298 K); here the error of the E_S compared is 1–2 kcal mol^{-1} (provided that the same additive scheme is used to calculate the ΔH_f° of the unstrained molecules).

(c) The difference between the contributions of the energies $p\Delta V$ to ΔH_f° for the cyclic compound and for the corresponding unstrained compound can be readily found from the relation $\Delta H_{f(G)}^\circ = \Delta U_{f(G)}^\circ + (1 - 1/2m)RT$ for compounds having the general formula C_nH_m. The difference between the $p\Delta V$ is incorporated in the E_S, where it is not constant (0.6 kcal mol^{-1} for cycloalkanes and 1.2 kcal mol^{-1} for bicycloalkanes) and will be eliminated in comparing the E_S in a given series of compounds.

Next, a comparison will be made of the conventional values of E_S, obtained as differences between the experimental and calculated $\Delta H_{f(G)}^\circ$ [see Eqn.(2)] or calculated with the aid of a mechanical model[17,18] in the few instances when no experimental ΔH_f° are available.

The experimental values of ΔH_f° and the strain energies E_S presented below are expressed in kcal mol^{-1} and refer to 298.15 K. The errors in ΔH_f° are expressed in terms of a 95% confidence interval and are given in round brackets. For example $\Delta H_{f(G)}^\circ$ for cyclopropane is 12.74(12) kcal mol^{-1}, i.e. in this case the error of the determination is 0.12 kcal mol^{-1}. In those cases where there are no experimental enthalpies of evaporation ΔH_v°, they were estimated from the Klages relation[28] in order to obtain ΔH_f° for the gaseous state (the latter quantities are listed in the Table without an indication of the error).

2. Geometrical Parameters of the Molecules

The steric disposition of the atoms in the molecules can be described unambiguously by specifying the internuclear distances r (the less rigorous term "bond length" is frequently used), the valence angles α, and the dihedral angles τ. The most accurate measurements of these molecular parameters are made in the gas phase by electron diffraction[13,29] and microwave spectroscopy[13,30]. The two methods yield geometrical parameters having a different physical significance and different indices and differing by an amount greatly exceeding the experimental error[31-33]. X-Ray diffraction analysis yields a third variety of geometrical parameters; therefore, in comparing data obtained by different methods, account must be taken of these differences.

However, even within the limits of each of the first two methods—electron diffraction and microwave spectroscopy—there exist a wide variety of parameters having a different significance. Readers wishing to make independently accurate comparisons of the internuclear distances should refer to the literature indicated above on the stereochemistry[13,30-33] and to the original studies. A rigorous comparison implies the employment of geometrical parameters of only one type within the limits of a given physical method.

In electron diffraction studies the final data are not presented in a unique manner and the authors quote distances designated by the symbol r_g or r_a. They are related by the equation

$$r_g = r_a + u^2/r_a ,$$

where u is the amplitude of the vibrations of pairs of atoms. The correction term u^2/r_a can be usually readily calculated and it amounts to 0.002 and 0.006 Å for the C–C and C–H bonds respectively. Tables 4–9 (see below) present data taken directly from original communications without indication of the type of distance. The only exception has been made for cycloalkanes, in which all the distances have been recalculated on the r_g basis to ensure a consistent comparison.

The distances designated by the symbols r_0 and r_s can be obtained from microwave data. They are not simply related and there are no simple relations between them and the electron diffraction parameters r_g and r_a.

The valence angles quoted in electron diffraction studies are believed to be the most reliable if they have been calculated taking into account the correction for the contraction effect[31]. Neglect of this correction can distort the valence angles by several degrees. The corrections are calculated on the basis of the theory of vibrations, provided that the force field of the molecule is known (for references to the last studies in this field, see Mastryukov and Dorofeeva[34]). The valence angles corrected for the contraction effect are designated by the symbol Φ_α in order to show that they refer to a geometrically self-consistent r_α structure, in contrast to the r_g and r_a structures.

We shall now proceed to the description of the comparison of the geometrical parameters carried out to find correlations with E_S. For this purpose, it is desirable to employ a simplified equation for the calculation of the strain energy E_S within the framework of the mechanical model (for more complex versions of the equation, see the relevant communications[18-21]):

$$E_s = E(r) + E(\alpha) + E(\tau) + E_{nv} = \\ = \frac{1}{2}K_r(r - r_0)^2 + \frac{1}{2}K_\alpha(\alpha - \alpha_0)^2 + \frac{1}{2}K_\tau(1 + \cos 3\tau) + E_{nv} \qquad (3)$$

Here each term refers to individual components of the strain mentioned previously: the deformation of the distances (r), the valence angles (α), and the dihedral angles (τ) and also the energies of non-valence interactions E_{nv}. The reference values are designated by the subscript 0.

It follows from Eqn.(3) that the strain energy is a complex function of many variables and by an empirical comparison one can only hope to find a parameter (or parameters) on which the E_S for a series of molecules with similar structures depend preferentially. For this purpose, it is necessary to analyse three pair combinations: E_S–r, E_S–α, and E_S–τ. We shall not consider the non-valence interactions in quantitative terms and shall confine ourselves to referring to the system of van der Waals radii[35], which are usually resorted to for comparisons of this kind.

Inspection of Eqn.(3) shows that, for example, in the case of internuclear distances a linear correlation is to be expected in terms of the variables E_S and $n(r - r_0)^2$, where n is the number of deformed bonds. This is also true of the valence angles. However, tests have shown that the simplest relations of the type E_S–$(r - r_0)$ and E_S–$(\alpha - \alpha_0)$ are much more convenient and we shall henceforth employ these.

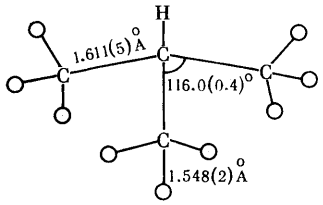
The second general observation about Eqn.(3) concerns the choice of the reference values of r_0 and α_0. In the mechanical model these quantities are empirical parameters without physical significance and are selected to ensure the best agreement between the calculation and experiment. We prefer to employ geometrical data for the reference molecules investigated. Admittedly in most instances such choice is not of fundamental importance, since the relative changes in $r - r_0$ and $\alpha - \alpha_0$ are necessary only for a qualitative derivation of a correlation with E_S, and the final quantitative characteristics, i.e. the correlation equations, have been usually derived not for the relative but for the absolute values of the geometrical parameters. The correlation equations make it possible in their turn to estimate independently certain values of r_0 and α_0 (see Section III).

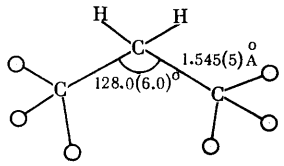
The selection of the reference values for the dihedral angle τ, which should be 60° for the *gauche*-orientation and 180° for the *trans*-orientation in acyclic systems, presents a special difficulty[36]. However, cyclisation distorts these values so much that they become of little practical use for a comparison. Furthermore, in the majority of structural studies there is simply no explicit information about the dihedral angles. For these reasons, we confined ourselves to comparing certain dihedral angles in repeating fragments of similar molecules.

As already mentioned, the most suitable standard for saturated hydrocarbons is a normal chain with the *trans*-disposition of all the C–C bonds, although at the usual temperatures there is also a considerable amount of other conformers. Electron diffraction studies on alkanes ranging from ethane to n-heptane established that the average parameters of these molecules are appreciably constant and we shall use them henceforth for the comparison: the average distance r_g(C–C) = 1.533(1) Å† and the average valence angle ∠C–C–C = 112.6(0.1)°.[37,38] More detailed information about the structures of different hydrocarbons can be found in the book of Volkov et al.[13]

A recent investigation[39] showed that the above constancy of the C–C bond lengths breaks down on passing to higher alkanes. Thus the distance for n-$C_{16}H_{34}$ is 1.542(4) Å, which has been attributed to the influence of non-valence interactions. A reinvestigation of n-C_4H_{10} [40] taking into account the contraction effect led to a more accurate C–C–C valence angle, equal to 113.8(0.4)°. We shall use the previous average value if only because in the majority of studies on cyclic hydrocarbons quoted here such corrections were not introduced.

Since the entire subsequent data refer to cyclic hydrocarbons, in conclusion of this section we shall present examples of strained acyclic molecules as an illustration. In such systems the strain increases with increasing branching of the chain, which is particularly notable for the t-butyl group. When two such groups are linked together, the distance between them is significantly increased and reaches 1.582(10) Å.[41] The greatest C–C distance (1.611 Å) has been recorded in the $(t\text{-}C_4H_9)_3CH$ molecule[42] and in the similar molecule of $(t\text{-}C_4H_9)_2CH_2$ [43] the C–C–C angle is appreciably increased. The structural data for these two unusual molecules are presented below (the methyl group is illustrated by a circle).





†As in the representation of the thermochemical data, here and henceforth the experimental errors referring to the last decimal places are given in round brackets, i.e. in this instance r_g = 1.533 ± 0.001. A more detailed form of notation is usually employed for angles, i.e. 112.6(0.1)°, although a formulation of the type 112.6(1)° can also be encountered in the literature.

The strain has also distorted the conformational characteristics of the butyl and methyl groups for which the deviations of the dihedral angles $\Delta\tau$ from the staggered orientation, which serves as the starting point of the calculation ($\tau = 0°$), are presented:

Molecule	$(t\text{-}C_4H_9)_3CH$	$(t\text{-}C_4H_9)_2CH_2$
$\Delta\tau$ (C_4H_9)	10.8 (0.5)°	15.1 (6.0)°
$\Delta\tau$ (CH_3)	18.0 (6.0)°	13.2 (7.0)°

3. The Spin–Spin Coupling Constants

In the literature on the NMR spectroscopy of organic compounds a considerable number of publications (including review publications) are devoted to the discussion of the question of the correspondence between the spin–spin coupling constant (SSCC) and the structural, conformational parameters of the molecule[44–74]. The influence of molecular structure on the SSCC between the nuclei of like and unlike atoms, both linked directly and separated from one another, has been investigated. In connection with the development of ^{13}C NMR spectroscopy, there has been a growth of interest in recent years in the study of the SSCC between the carbon nuclei constituting the skeleton of an organic molecule. These constants are significantly smaller than the corresponding SSCC for protons, but this deficiency is compensated by the simplicity of the observation of the J_{C-C}.[71,75–77].

At the same time one should note that few systematic data, enabling one to trace the "geometry–SSCC" relation for a series of structurally similar compounds, are available. Among cyclic hydrocarbons, the SSCC for vicinal protons $^3J_{H-H}$ (the coupling constants of the ^1H nuclei via three bonds) and the coupling constants for the ^{13}C and ^1H nuclei via one bond $^1J_{^{13}C-H}$ (obtained either from high-resolution ^{13}C NMR spectra or by analysing the ^{13}C satellites in proton spectra), for which definite correlations with the structure have been established (see below), constitute an exception in this respect.

In this review we shall not be concerned with the theoretical aspects associated, in particular, with the mechanism of the spin–spin coupling, to which due attention has been devoted in the series of reviews quoted here. We shall only note that the true cause of the changes in the SSCC is still not altogether clear. They can be caused by an alteration of the *s* character of the corresponding orbital and hence can serve as a measure of the *s* character of the bond. (Minimum values of the $^1J_{^{13}C-H}$ constant are characteristic of carbon atoms with sp^3, sp^2, and *sp*-hybridisations, amounting to ~125, 156, and 250 Hz respectively.) Formulae linearly relating the degree of *s* character of the hybrid orbital of the carbon atom in the C–H bond to the $^1J_{^{13}C-H}$ constant have been proposed and have been frequently revised[44,78–86]. At the same time there exists the view that it would be premature to establish a quantitative correlation between the constant $^1J_{^{13}C-H}$ and the degree of *s* character and that it would be more correct to regard $^1J_{^{13}C-H} \cong 125$ Hz as a characteristic of tetracoordinate carbon with a tetrahedral environment[86,87].

The change in the SSCC may be a consequence of the change in the length of the corresponding bond caused by the deformation of the angles and the diminution of repulsive interactions[86]; in particular, an increase of the constant $^1J_{^{13}C-H}$ should then be expected. However, certain experimental and calculated data have shown that there is no direct relation between these quantities[48,58,67,68,79]. Despite the difficulty of interpretation, the correlation between the SSCC and the deformation of the structure is believed to have been reliably established[70]. However, one must not forget the definite (known) inaccuracy of the relations established is due to the fact that one of the parameters compared (SSCC) characterises the substance in the liquid state and the other (structural parameter) characterises the substance in the gaseous (or crystalline) state. One must also take into account the influence of the steric interactions of the neighbouring groups on the SSCC and hence the possibility of employing the observed correlations only within the limits of a series of isotypical compounds.

In this study we have analysed the "geometry–SSCC" relation on the basis of new experimental results or results which have been revised in recent years. We used mainly the constants $^1J_{^{13}C-H}$ and $^3J_{H-H}$, whose values for cyclic hydrocarbons are most systematic, as mentioned above. Certain bridged bicyclic hydrocarbons are an exception; successive changes in the SSCC between vicinal protons ($^2J_{H-H}$) and between protons via four bonds ($^4J_{H-H}$) have been described for these compounds.

II. CORRELATION BETWEEN THE STRAIN ENERGY, THE GEOMETRICAL PARAMETERS, AND THE SPIN–SPIN COUPLING CONSTANTS

1. Cycloalkanes

(a) Correlation between the Strain Energy and the Structural Parameters

The structural data for cycloalkanes and the strain energies E_S are listed in Table 4. The following dimensions are used in Tables 4–9 and in the text: kcal mol^{-1} for E_S, Å for the internuclear distance, degrees (°) for the valence and dihedral angles, and Hz for the SSCC.

The conformational characteristics of these hydrocarbons are distinguished by their wide variety and are not susceptible to analysis on a single basis. Indeed, cyclopropane is a rigid system, cyclobutane is bent by an angle of 26°#, there is pseudorotation in cyclopentane, and cyclohexane exists in the chair conformation with a torsional angle of 54.5°. The conformations of cycloheptane, cyclooctane, and cyclodecane are also comparatively unrelated to the conformations of the preceding homologue. Since it is difficult to put forward a single scheme for the comparison of the dihedral angles in the above molecules, we shall confine ourselves to the consideration of the internuclear distances r_g(C–C) and the C–C–C valence angles. These geometrical parameters will be considered in much more detail for cycloalkanes than for other cyclic compounds, firstly in order to illustrate the approach employed, which is to a large extent repeated in the subsequent sections of the review and, secondly, because of the unusual nature of the results obtained for the cycloalkanes themselves.

#The view has been established in the literature that the four-membered ring of cyclobutane is bent by an angle of ~35°.[104,105] In the latest electron-diffraction study it has been shown that allowance for the pendulum shifts of the methylene groups (for a more detailed description of this effect, see Mastryukov et al.[106]) leads to a significant decrease of the non-planarity of the cyclobutane ring, which confirms the results of non-empirical quantum-chemical calculations[107].

Table 4. The enthalpies of formation, strain energies, structural parameters, and SSCC of cycloalkanes*.

Molecule	ΔH_f°(L) (expt)	ΔH_f°(G) (expt)	ΔH_f°(G) (calc.)	E_s	r_g (C–C)	r_g (C–H)	∠C–C–C,	∠H–C–H	Ring shape	$^1J_{^{13}C-H}$
C_3H_6	—	12.74 (12)	−14.85	27.6	1.512 (2) [89]**	1.095 (3)	60.0	114.1 (1.0)	planar	161 [44]; 162 [97, 98]; 160.45 [99]
C_4H_8	0.88 (12)	6.79 (12)	−19.80	26.6	1.551 (3) [90]	1.109 (6)	88.5	107 (3)	bent by 26(3)°	134 [44]; 136 (1) [97]
C_5H_{10}	−25.60 (17)	−18.74 (19)	−24.75	6.0	1.546 (1) [91]	1.113 (1)	104.1	106.0	non-planar; pseudorotation	128 [44]; 131 (2) [97]; 128.221 (0.005) [100]
C_6H_{12}	−37.36 (07)	−29.47 (07)	−29.70	0.2	1.536 (2) [92, 93]	1.121 (4)	111.4 (0.2)	107.5 (1.5)	chair with a torsional angle of 54.9(0.4)°	123 (124) [44]; 127 (2) [97]; 125.00 [101]; 124.56 [102]
C_7H_{14}	−37.45 (12)	−28.25 (14)	−34.65	6.4	1.540 (1) [94]	1.118 (3)	115.3 (0.3)		twisted chair***	122 [44]; 127 (2) [97]
C_8H_{16}	−40.08 (22)	−29.73 (22)	−39.60	9.9	1.542 (5) [95]	1.113 (15)	116.6	108.0	mixture of conformers	123 [44]; 126 (2) [97]
C_9H_{18}	−43.31 (22)	−31.74 (38)	−44.55	12.8						125 (2) [97]; 124 (3) [103]
$C_{10}H_{20}$	−49.40 (22)	−36.88 (36)	−49.50	12.6	1.545 (3) [96]	1.115 (3)	116.1 (1.1)	105.4	boat-chair-boat****	118 [44]; 121 (3) [103]; 126 (2) [97]

*The experimental values of ΔH_f° were taken from Pedley and Rylance[88].

**In this and subsequent Tables the references indicated for one of the geometrical parameters refer to all the structural data presented.

***The content of the main conformer was 76 ± 6%.

****The content of the main conformer was 49 ± 3%.

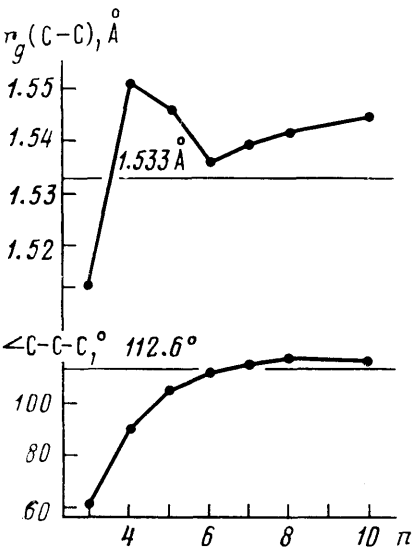


Figure 1. Variation of the C–C internuclear distances r_g and the C–C–C valence angles in the cycloalkanes C_nH_{2n} with ring size n. The horizontal lines correspond to reference values.

The distances r_g(C–C) and the valence angles in the cycloalkanes investigated are illustrated in Fig. 1. The range of variation of the distances (1.512–1.551 Å, i.e. ±2.5% relative to the average value) is significantly smaller than the range of variation of the valence angles (60–116.6°, i.e. ±64% relative to the average value). However, the variation of the internuclear distances is more complex, while the variation of the valence angles has the simpler form of curves with saturation§. The variation of the geometrical parameters of cycloalkanes expressed in this direct form has no analogy whatever with the variation of the E_S for these compounds illustrated in Fig. 2.

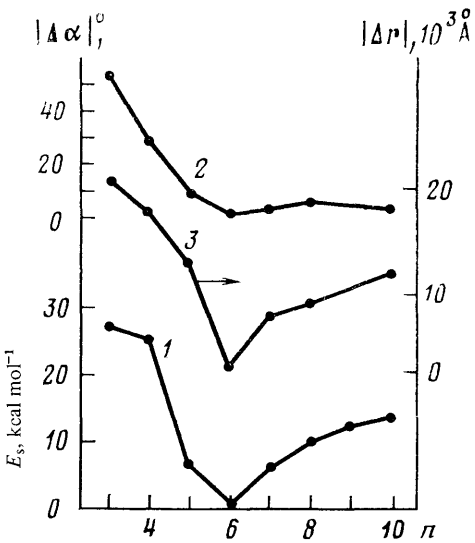


Figure 2. Variation of the strain energy E_S (curve 1) and of the differences $\Delta\alpha = |112.6° - \alpha|$ (curve 2) and $\Delta r = |1.533 - r| \times 10^3$ (Å) (curve 3) in the cycloalkanes C_nH_{2n} with ring size n.

§It is of interest to note that the introduction of a heteroatom into the cyclic system does not alter significantly the features found for hydrocarbons[108].

As mentioned above, the strain energies E_S must be compared with the deviations of the geometrical parameters of the molecule under consideration from the reference values. Since the symmetrical deviations from the reference values must make the same contributions to the E_S (in the mechanical model this phenomenon is described by Hooke's law), the absolute differences are employed for the comparison with the E_S: $\Delta r = |1.533 - r| \times 10^3$ Å for the C–C distances and $\Delta\alpha = |112.6° - \alpha|$ for the C–C–C angles. These differences are in fact illustrated in Fig. 2. It is quite evident that even such relative geometrical parameters reproduce correctly in qualitative terms the decrease of E_S on passing from C_3H_6 to C_6H_{12} with a subsequent increase on further ring expansion.

Fig. 2 shows that the curve illustrating the variation of the internuclear distances closely imitates the form of the E_S curve. A direct confirmation of this observation follows from the correlation equations

$$E_s = -5.74 + 1.56\ \Delta r\ , \qquad (4)$$

$$E_s = 6.19 + 0.48\ \Delta\alpha\ , \qquad (5)$$

obtained by the least squares method and presented in a graphical form in Figs. 3 and 4. These relations clearly show that the values of E_S for cycloalkanes are very closely related to the changes in the internuclear distances in these molecules.

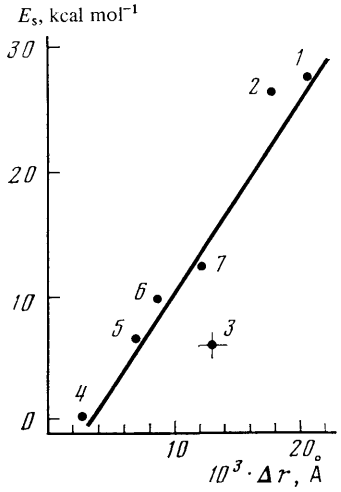


Figure 3. Variation of the strain energy E_S with Δr for different hydrocarbons: *1*) C_3H_6; *2*) C_4H_8; *3*) C_5H_{10}; *4*) C_6H_{12}; *5*) C_7H_{14}; *6*) C_8H_{16}; *7*) $C_{10}H_{20}$. The error in the measurement of the internuclear distances (±0.001 Å) and the approximate error in the estimation of E_S (±1.5 kcal mol^{-1}) for cyclopentane as an example are indicated by horizontal and vertical lines; straight line—calculation by Eqn. (4).

As a consequence of the satisfactory linear relation between E_S and Δr, Eqn. (4) can be used for quantitative estimates of the C–C distances in the hydrocarbons for which only thermochemical data are available. For example, the rg(C–C) = 1.545 Å distance has been estimated from E_S in C_9H_{18}¶.

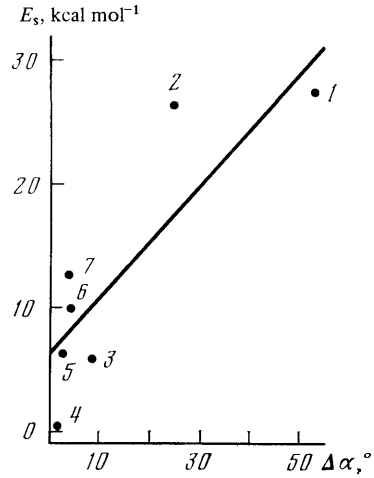


Figure 4. Variation of the strain energy with $\Delta\alpha$: *1*)–*7*) see Fig. 3; straight line—calculation by Eqn. (5).

The preferential correlation of E_S with the deformations of the internuclear distances rather than the valence angles conflicts with the generally accepted hypothesis that the values of E_S for cycloalkanes are mainly determined by the angular Baeyer strain. The same conflict obtains also in the mechanical model: a change in distances is believed to be so unfavourable energetically that in some calculations this effect is simply neglected[9].

In more accurate calculations[17–21] it is assumed that a 10% deformation of the C–C distances (for example, a change from 1.54 to 1.70 Å) is accompanied by a change in the strain energy by only 3.1 kcal mol^{-1}.[18] The result obtained in the above study shows that the changes in the C–C distances in the range 1.512–1.551 Å are satisfactorily correlated with the changes in E_S in the range 0.2–27.6 kcal mol^{-1}. It is noteworthy that the cyclopropane molecule does not deviate from this relation, although it has the shortest bond. The minimum C–C distance in this compound has been interpreted by some workers within the framework of the special concept of "bent bonds".[13,109]

We do not believe that the above contradictions indicate deficiencies of the computational procedure based on the mechanical model, because our treatment is extremely limited and empirical, as already mentioned. Attention need only be drawn to the fact that the analysis of the direct dependence of E_S on the geometrical parameters of cycloalkanes

¶The structural data for C_7H_{14} have been published only recently[94] and the initial version of Eqn. (4) was therefore derived without taking them into account and had the form $E_S = -6.37 + 1.59\ \Delta r$. On substituting the value of E_S for cycloheptane in this expression, it is possible to calculate rg(C–C) = 1.541 Å, which is larger than the experimental value only by 0.001 Å.

can yield an interesting and unusual result, which was not discussed previously and which can be used to estimate internuclear distances from thermochemical data (or conversely). Cycloalkanes occupy a special position, because the strain energies of cycloalkanes and bicyclic hydrocarbons are better correlated with the deformation of the valence angles (as will be seen from the exposition below).

We shall not deal with the H–C–H angles whose deformation also contributes to the strain energy, because the angles ∠C–C–C (α) and ∠H–C–H (β) vary in a concerted manner[110] in accordance with the linear equation

$$\beta = 126.1 + 0.17\,\alpha \ .$$

As a result of this relation, the behaviour of the difference $\Delta\alpha$ illustrated in Fig. 4 should reflect correctly the overall deformation component of the strain energy in cycloalkanes.

As already mentioned in the introduction, substituted cyclic hydrocarbons will not be considered systematically. The only exception was made for hydrocarbons of the cyclopropane series. In recent years extensive experimental data have accumulated for the ΔH_f° of cyclopropanes which have not been surveyed. Using these data, we considered the influence of the introduction of substituents of different types on the E_S for the three-membered ring. The data in Table 5, which lists the values of ΔH_f° and E_S for substituted cyclopropanes and cyclopropenes, show that E_S is constant (27–28 kcal mol^{-1}), within the limits of the error of the determination, for all saturated hydrocarbons with the exception of the seventh and eighth compounds†. The strain energy E_S of alkenyl derivatives of cyclopropane with the double bond separated from the ring by a σ-bond is close to E_S for cyclopropane itself, which indicates either the absence of an effect of $p-\pi$ conjugation or its very small magnitude. The introduction of an exocyclic or endocyclic double bond greatly increases E_S for the three-membered ring.

The estimated strain energy per trigonal atom in cyclopropene, evaluated as half the difference between the values of E_S for cyclopropene and cyclopropane, is 13.1 kcal mol^{-1}. Subsequent calculation of E_S for methylenecyclopropane, defined as the sum of E_S for cyclopropane and 13.1 kcal mol^{-1}, leads to 40.7 kcal mol^{-1}, which fully agrees with the value calculated from the experimental $\Delta H_{f(G)}^\circ$ for methylenecyclopropane (Table 5). This agreement suggests that the contributions of the trigonal carbon atom (*endo*- or *exo*-) to the strain energy in the systems considered are approximately the same.

Thus the data presented show that the introduction of the substituents into the molecule hardly alters the overall strain energy. At the same time in approximate quantum-chemical calculations[116] a relatively strong steric interaction between the CH_3 groups is postulated.

(b) Correlation between the Structural Parameters and the SSCC

On the basis of the changes in the constants $^1J_{^{13}C-H}$ in the series of cyclic saturated hydrocarbons (ranging from cyclopropane to cyclododecane), a linear correlation was observed as early as 1963 between the SSCC and the angle ∠C–C–C, described by the equation[44]

$$^1J_{^{13}C-H} = 203 - 0.720\,\alpha \ . \qquad (6)$$

Using Foote's data[44], Mislow[57] derived a correlation equation expressing the dependence of the constants $^1J_{^{13}C-H}$ not on the angle α but on the interorbital angle α_{orb} (which reflects the state of hybridisation and is determined from the relation $\alpha_{orb} = 0.1340\alpha + 94.83$).[57] However, calculation of the above constant by Eqn. (6) using modern values of the geometrical parameters (Table 4) yields values of $^1J_{^{13}C-H}$ which differ appreciably in many instances from the experimental values.

Table 5. The enthalpies of formation and strain energies of substituted cyclopropanes and cyclopropenes.

Molecule*	$\Delta H_{f(L)}^\circ$ **	$\Delta H_{f(G)}^\circ$	E_S	References
	—	12.74 (12)	27.6	[88]
	0.41 (16)	5.8	27.7	[88]
	−5.92 (19)	0.8	27.6	[88]
	−7.97 (19)	−1.97 (30)	27.6	[88]
	−6.29 (16)	0.4	29.3	[88]
	−7.34 (19)	−0.9	28.0	[88]
	−22.99 (20)	−15.7	20.9	[88]
	−28.63 (22)	−20.6	23.7	[88]
	−21.57 (24)	−13.6	27.9	[88]
	−27.74 (40)	−18.5	28.0	[88]
	−46.14 (54)	−33.8	27.5	[88]
	22.9 (90)	30.9 (90)	27.3	[88]
	29.3 23.6 24.5 (20)	— — 31.3 (30)	— — 27.8	[111] [112] [113]
	14.51 (30)	22.4	27.4	***
	46.80 (50)	55.8	28.6	***
	62.40 (20)	69.8 (40)	26.7	[113]
	—	47.9 (40)	40.8	[88]
	—	94.6 (280)	—	[114]
	—	66.2 (60)	53.8	[88]
	—	58.2 (20)	53.7	[88]
	32.8 (50)	39.6 (110)	—	***

*R = CH_3, $R^1 = C_2H_5$, $R^2 = C_3H_7$, and $R^3 = C_6H_{13}$.

**Turner et al.[115] determined the enthalpies of hydrogenation of methylmethylenecyclopropane, ethylidenecyclopropane, and 1,2-dimethylcyclopropene in solution in acetic acid at 25 °C. We did not calculate the values of $\Delta H_{f(G)}^\circ$ from these data, because the differences between the enthalpies of evaporation and solution are unknown.

***S.M.Pimenov's data (Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1982).

†The ΔH_f° for 1,1,2-trimethyl- and 1,1,2,2-tetramethylcyclopropanes and vinyl-cyclopropane should be redetermined.

Fig.5 presents the changes in the constant $^1J^{13}C-H$, the C–C–C valence angles, the C–C internuclear distances, and the E_S (the data from Table 4) for the series of compounds considered on passing from cyclopropane to cyclododecane (the geometrical parameters of cyclononane have still not been determined). It shows that the SSCC vary almost in parallel with the variation of the C–C–C angle only.

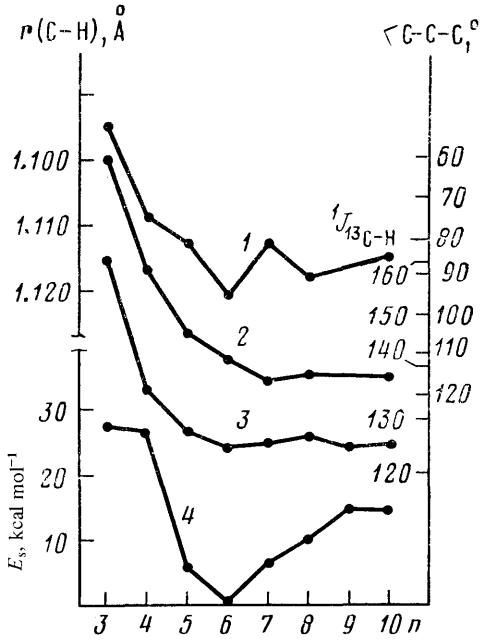


Figure 5. Variation of the C–H internuclear distances (curve *1*), the C–C–C valence angles (curve *2*), $^1J^{13}C-H$ (curve *3*), and E_S (curve *4*) in cycloalkanes with ring size *n*.

On the basis of the data presented, a linear relation was obtained between $^1J^{13}C-H$ and the C–C–C angle (α) for cycloalkanes ($^1J^{13}C-H = 195.7 - 0.632\alpha$), which, however, is characterised by a relatively small but appreciable scatter of the points. If the data corresponding to cyclopropane are disregarded in the calculation, then the above relations for the series of saturated cyclic hydrocarbons ranging from cyclobutane to cyclohexane fit satisfactorily on a straight line. The relation between $^1J^{13}C-H$ and ∠C–C–C for the series of cycloalkanes is best described by the parabolic equation (Fig.6)

$$^1J_{^{13}C-H} = 0.0073\,\alpha^2 - 1.963\,\alpha + 251.715 \quad . \qquad (7)$$

On the basis of the observed relation between E_S and the C–C distance [Eqn.(4)], the unknown average internuclear distances in cyclononane were estimated previously. Using Eqn.(7), it is also possible to find the average C–C–C angle in this hydrocarbon; it amounts to 111° (in agreement with the data in Table 4). Eqn.(7) satisfies the corresponding parameters of propane[117] and, which is particularly interesting, strained compounds such as bicyclo[2,2,1]-heptene and bicyclo[2,2,1]hepta-2,5-diene (for the $^1J^{13}C(7)-H$ and the corresponding angles, see Table 9 below).

2. Cycloalkenes

(a) Correlation between the Strain Energy and Structural Parameters

The structural data and the strain energies E_S for cycloalkenes are presented in Table 6. *cis*-But-2-ene serves as a suitable standard for comparisons in this series of compounds[131]. The required parameters of this molecule are the C–C distance [1.506(2) Å], the C = C distance [1.346(3) Å], and the C–C = C angle [125.4(0.4)°]. We shall consider initially the C–C and C = C distances. Comparison with the distances in the standard reveals the following features: cyclopropene should be just as strained as cyclohexene, but both these compounds are less strained by a factor of ~1.5 than cyclo-octene. The data presented in no way agree with the E_S curve in Fig.7.

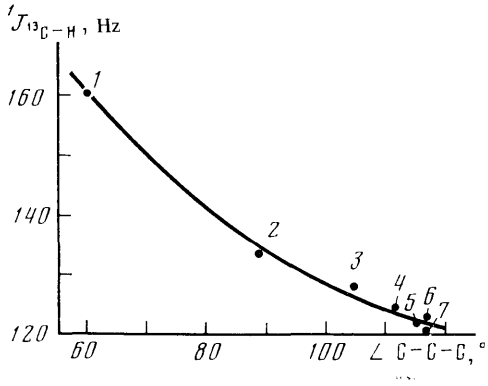


Figure 6. Variation of $^1J^{13}C-H$ with the C–C–C angle for cycloalkanes: *1*)–*6*) see Fig.3; *7*) C_9H_{18}; curve—calculation by Eqn.(7).

On the other hand, there is a satisfactory agreement between this curve and the variation of the C–C = C (α_1) ($\Delta\alpha_1 = 125.4 - \alpha_1$) and the C–C–C ($\alpha_2$) ($\Delta\alpha_2 = 112.6 - \alpha_2$) angles, illustrated in Fig.7. Since the differences $\Delta\alpha_1$ and $\Delta\alpha_2$ have non-alternating signs, the conclusions are independent of the type of standard within the limits of a single sequence of molecules. In this case it is more useful to find correlation equations using the geometrical parameters themselves rather than the above differences#. For the above angles, the equations assume the following form:

$$E_S = 111.2 - 0.895\,\alpha_1 \quad . \qquad (8)$$

$$E_S = 100.6 - 0.894\,\alpha_2 \quad . \qquad (9)$$

Their graphical representation is illustrated in Fig.8. The parallel arrangement of the straight lines obtained on the basis of Eqns.(8) and (9) is striking. Thus, in contrast to cycloalkanes, a correlation of the strain energy only with the deformations of valence angles is characteristic of their unsaturated analogues.

#We shall adhere to a similar approach henceforth; for a qualitative determination of correlations involving E_S, the relative changes in the geometrical parameters are usually employed, but in the final equations the structural parameters are used directly.

Table 6. The enthalpies of formation, strain energies, structural parameters, and SSCC of cycloalkenes.

Molecule	$\Delta H^\circ_{f(L)}$	$\Delta H^\circ_{f(G)}$	E_s	CC and CH bonds	Valence angles	Dihedral angles	$^1J_{^{13}C-H}$	$^3J_{H-H}$
	—	66.23 (60)	53.3	1—2 1.304 (3) [119, 120] 1—3 1.519 (2) 1—H 1.077 (12) 3—H 1.112 (15)	2—1—H 132.9 (2.5)	—	226 [127]; 220 [128]; 228.2 [129]	1.3 [127, 129]
	—	37.45 (36)	29.8	1—2 1.342 (5) [121] 1—4 1.517 (5) 3—4 1.566 (5) 1—H 1.083 (5) 3—H 1.094 (5)	1—2—3 94.2 (0.5) 2—3—4 85.8 (0.5) 2—1—H 133.5 (0.5) H—3—H 109.2 (0.5) 4—3—H 114.5 (0.5)	—	170 [45, 130]	2.7 [46]; 2.85 [130]
	1.10 (41)	7.81 (41)	5.1	1—2 1.546 (35) [122] 2—3 1.519 (30) 3—4 1.342 (10) C—H$_{av}$ 1.098 (6)	2—3—4 111.0 (1.2) H—1—H 104.8 H—2—H 101.8 3—4—H 143.5	2—1—5 / 2—3—4—5 28.8 (2.5)	160 (1) [47]; 161.6 [48]	5.1 [46]; 5.4 (0.1) [47]; 5.57 [48, 49]
	—9.11 (10)	—1.10 (12)	1.1	1—2 1.335 (3) [123—125] 2—3 1.504 (6) 3—4 1.515 (20) C—H 1.093 (15)	1—2—3 123.5 2—3—4 112.1 3—4—5 111.0	1—2—3—4 —15.2 2—3—4—5 44.9 3—4—5—6 —60.2	157 [47]; 158.4 [48]	8.8 [46]; 9.6 [47]; 10.11 (0.05) [48, 49]
	—	—2.25 (22)	4.9	—	—	—	156.2 [48]	10.8 [46]; 11.02 [48]
	—	—6.45 (26)	5.7	1—2 1.332 (3) [126] 2—3 1.499 (8) 3—4, 4—5, 5—6 1.549 (2) 3—H 1.110 (2) 1—H 1.103	1—2—3 121.9 (0.8) 2—3—4 104.6 (0.4) 3—4—5 113.8 (0.4) 4—5—6 118.8 (0.6) 2—1—H 118.4 (2.0) H—C—H 106.8 (1.7)	8—1—2—3 136.0 (0.4) 1—2—3—4 —91.1 (0.8) 2—3—4—5 54.2 (1.0) 3—4—5—6 —82.8 (0.6) 4—5—6—7 111.8 (1.0) H—1—2—H 177.6 (11.2)	156.0 [48]	10.3 [46]; 10.41 [48]

Note. Here and henceforth the atoms are numbered in accordance with data obtained in structural studies. The experimental values of ΔH°_f were taken from Pedley and Rylance[88]. The dihedral angles in this and subsequent tables are presented in a dual form. The first has the usual significance, for example, $\tau(1-2-3-4)$ denotes the angles between the planes drawn through the 1—2—3 and 2—3—4 carbon atoms. The second designation is in the form of a fraction in which the planes between which the angle is measured are indicated in the numerator and denominator.

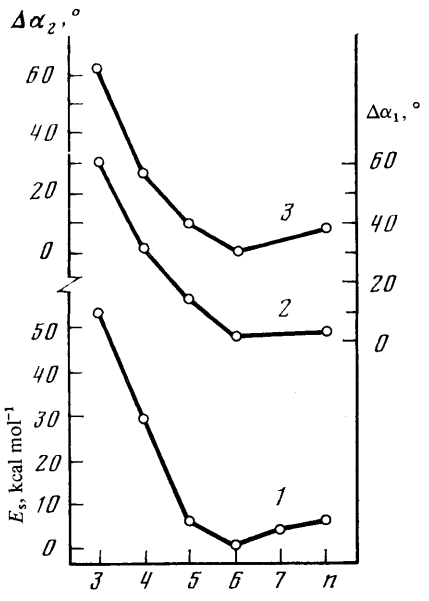


Figure 7. Variation of the strain energy E_S (curve 1) and the differences $\Delta\alpha_1 = 125.4° - \alpha_1$ (curve 2) and $\Delta\alpha_2 = 112.6° - \alpha_2$ (curve 3) in the cycloalkenes C_nH_{2n-2} with ring size n.

(b) Correlation between the Structural Parameters and the SSCC

It is known that in the series of *cis*-cyclo-olefins there exists a definite relation between the SSCC of the vinyl protons and the ring size[45—48,50,56,68]. The change in the constant $^3J_{H-H}$ is more likely to be due to the local geometry about the double bond[45,46] (the C = C interatomic distances and the C = C—C and C = C—H angles) rather than the overall strain energy of the molecule. The empirical correlations derived by different investigators between the above constants and the C = C interatomic distances are similar and correspond to an increase of the constant $^3J_{H-H}$ by ~0.6—0.7 Hz as the C = C bond length diminishes by 0.02 Å.[68] The comparisons of the above relations with experimental data have shown, however, that there is no direct relation between the constants $^3J_{H-H}$ and the C=C bond length[48,49,68]. Thus the change in the C = C internuclear distance from 1.342 Å in cyclobutane to 1.332 Å in cyclo-octene should have corresponded to an increase of the constant $^3J_{H-H}$ by ~0.3 Hz, while in reality the difference between the constants is ~7.5 Hz.

The relation between the constants $^3J_{H-H}$ and the C = C—H angles has been shown by the analysis of the study of Cooper and Manatt[48] to be close to the predicted theoretical relation[55], the sensitivity of the SSCC to the change in ∠C = C—H being particularly notable for angles close to 120°. The C = C—H angle is found from the C = C—C angles, which

are more readily determined experimentally, using the relation $\angle C = C-H \cong (360 - \angle C = C-C)/2$. Calculation of the dependence of the constants $^3J_{H-H}$ on the C = C–C and C = C–H angles for *cis*-buta-1,3-diene (for changes in the angles from 108° to 123° and from 114° to 124° respectively) showed that the size of the angles has an appreciable influence on the constant; the dependence of $^3J_{H-H}$ on the C = C–C angle is more explicit than that of the C = C–H angle[68].

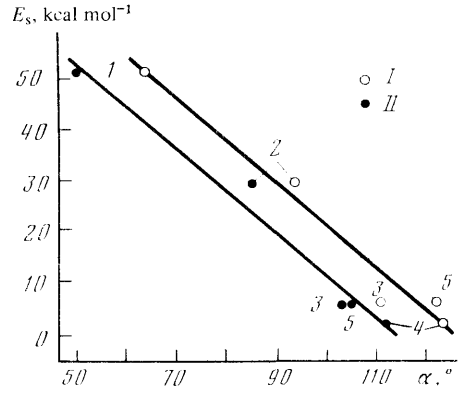


Figure 8. Variation of the strain energy with the C–C = C (*I*) and C–C–C (*II*) valence angles for different hydrocarbons: *1*) C_3H_4; *2*) C_4H_6; *3*) C_5H_8; *4*) C_6H_{10}; *5*) C_8H_{14}; *I*) calculated by Eqn.(8); *II*) calculated by Eqn.(9).

Comparisons have also been made between the structural parameters of cyclo-olefins and the constants $^1J_{^{13}C-H}$.[52,54,72] A linear relation has been established between the constant $^1J_{^{13}C-H}$ and the C = C–C angle for a series of unsaturated compounds of different types[54]. (However, the points corresponding to cyclobutene and cyclopentene do not fit on the resulting straight line.)

Fig.9 presents the variation of $^1J_{^{13}C-H}$, $^3J_{H-H}$, the C = C–C angles, the C = C distances, and the strain energies E_S (according to the data in Table 6) in the series of compounds investigated ranging from cyclopropene to cyclo-octene. It is seen that the SSCC and the C = C–C angle vary in parallel, the parallelism breaking down on passing from cyclopropene to cyclobutene. There is no correspondence whatever between the variations of both SSCC and the C=C bond length; nor is there a full correlation (particularly of the constant $^1J_{^{13}C-H}$) with the strain energies E_S.

The linear equations describing the relations between the SSCC and $\angle C = C-C$ (α) ($^1J_{^{13}C-H} = 277.5 - 1.014\alpha$; $^3J_{H-H} = -9.88 + 0.1556\alpha$) do not reflect the observed relation in a sufficiently clear-cut manner. (As for cycloalkanes, the linear correlation holds when data corresponding to the three-membered unsaturated ring are rejected in the calculation.) The dependence of the SSCC on $\angle C = C-C$ (α) has been studied most completely and in this instance is described by the parabolic equations (Figs.9 and 10)

$$^1J_{^{13}C-H} = 0.0195\alpha^2 - 4.720\alpha + 443.327 \quad , \qquad (10)$$

$$^3J_{H-H} = 0.0039\alpha^2 - 0.579\alpha + 22.465 \quad . \qquad (11)$$

The question of the reason for the deviations from the linear relation of the corresponding parameters of both saturated and unsaturated three-membered rings (if the accuracy of the determinations of the quantities compared is assumed to be adequate) still remains open. Owing to the lack of systematic, uniform data for a large number of the hydrocarbons considered (in the series of cycloalkenes the entire calculation is in fact based on the parameters for 4–5 compounds), it is difficult to reach a definite conclusion. Possibly the deviations are caused by the extremum values of the geometrical parameters or a significantly different hybridisation of the carbon atom in three-membered cyclic compounds, which occupy an intermediate position between saturated, unsaturated, and acetylenic hydrocarbons.

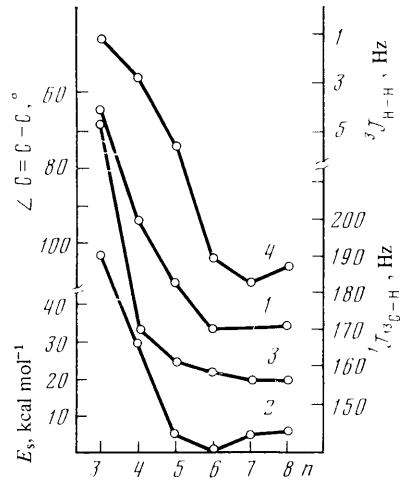


Figure 9. Variation of the C = C–C valence angles (curve *1*), E_S (curve *2*), $^1J_{^{13}C-H}$ (curve *3*), and $^3J_{H-H}$ (curve *4*) in cycloalkenes with ring size *n*.

It is noteworthy that Eqn.(10) is also characteristic of certain other unsaturated compounds, particularly of ethylene[117], cyclohexa-1,4-diene[67], cyclo-octatetracene[52], bicyclo[2,2,1]hept-2-ene[118], and bicyclo[2,2,2]octa-2-ene[48], while correlation (11) holds satisfactorily both for the above hydrocarbons and in addition for cyclopenta- and cyclohexa-1,3-dienes[67] and cycloheptatriene[68].

3. Cyclo-1,3-Dienes

Few data are available for cyclopolyenes and they are not susceptible to analysis on a common basis (Table 7). In agreement with previous observations, the strain energy E_S is a minimum for the six-membered ring, although the transition from the five- to the six-membered system is accompanied by only a slight decrease of E_S, amounting to 0.6 kcal mol^{-1} (the analogous decrements in the series of cycloalkanes and cyclo-olefins are 5.8 and 4.0 kcal mol^{-1} respectively).

It follows from Table 7 that the main internuclear distances (C = C, =C–C=, and =C–C–) in the dienes considered are equal within the limits of experimental error. The only

notable change occurs in the valence angles on ring expansion. For example, the C = C–C(=) valence angle§ increases in the series of compounds considered (109.21°, 120.13°, 129.1°, and 129.0°), which does not agree with the variation of E_S. Thus, for the given class of compounds, it is so far impossible to discover the geometrical parameter which is most closely related to the changes in E_S or the SSCC $^3J_{H-H}$ of vinyl protons).

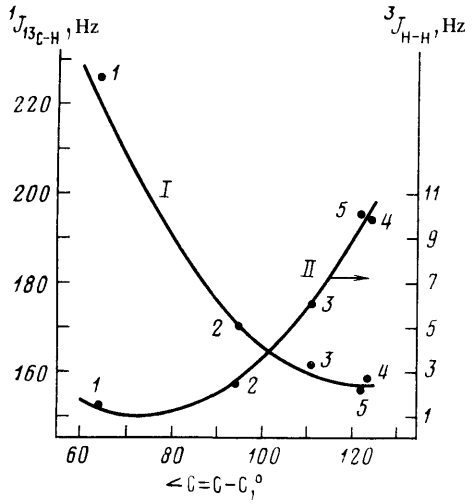


Figure 10. Variation of $^1J_{^{13}C-H}$ (curve *I*) and $^3J_{H-H}$ (curve *II*) with the C = C–C angles for C_nH_{2n-2} cycloalkenes; *1*)–*5*) see Fig.8; *I*) calculation by Eqn.(10); *II*) calculation by Eqn.(11).

4. Bicyclo[*n*,1,0]alkanes

(a) Correlation between the Strain Energy and the Structural Parameters

Thermochemical and geometrical data for bicyclo[*n*,1,0]-alkanes are compiled in Table 8. In their molecules there are several types of C–C distances which differ slightly from one another. The small differences between the C–C distances can be found accurately only by microwave measurements or by means of a combination of electron diffraction and spectroscopic data. The most interesting geometrical parameter in the above series of compounds is undoubtedly the length of the common C–C bond. The results of its measurement are available only for the first three representatives of the series, but they do not exhibit an appreciable correlation with the changes in the E_S of these compounds (Fig.11). This also applies to other individual C–C distances in these molecules.

The C–C–C valence angles in bicycloalkanes differ from those in the compounds considered previously by the presence of a tertiary carbon atom. The value of this angle for isobutane (110.8°) [154] was adopted as the reference value. The sum of the differences $\Delta\alpha = (110.8° - \alpha_1) + (110.8° - \alpha_2) + (110.8° - \alpha_3)$ was adopted as the measure of the strain in the three C–C–C angles around the tertiary carbon atom. The choice of the angles α_1, α_2, and α_3 is explained below in relation to bicyclo[1,1,0]butane:

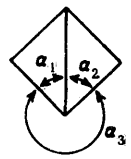


Fig.11 shows that the deformation of the angles about the tertiary carbon atom and the strain energy vary similarly in the series of condensed hydrocarbons and Fig.12 presents the variation of E_S as a function of the average angle $\angle C-C-C_{av} = \alpha_{av} = (\alpha_1 + \alpha_2 + \alpha_3)/3$. The corresponding equation is

$$E_s = 168.2 - 1.374\,\alpha_{av}\,. \qquad (12)$$

An analogous relation is obtained when account is taken of the C(1)–C(2)–C(3) valence angles (α) in a large ring, which are 60°, 89.5°, and 100.9° respectively according to calculations for the first three compounds in Table 8. The corresponding correlation equation is

$$E_s = 110.5 - 0.706\,\alpha\,. \qquad (13)$$

The dihedral angles θ at which the plane of the three-membered ring is inclined relative to the plane of the ring condensed with it have also been measured for the hydrocarbon investigated. The variation of these angles is not consistent with the variation of the E_S, as can be seen from Fig.13. Nor has a correlation been observed between E_S and the average C–C distances, which amount to 1.498, 1.529, 1.524, and 1.535 Å respectively for the saturated hydrocarbons of the bicyclo[n,1,0] series investigated (Table 8).

(b) Correlation between the Structural Parameters and the SSCC

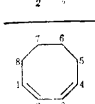
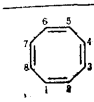
Few data are available for the SSCC for condensed bicyclic systems containing a three-membered ring. The geometrical and thermodynamic parameters of bicyclo[*n*,1,0]alkanes have been determined only for the first four members of the series. Fig.13 presents the dependence of the constant $^1J_{^{13}C-H}$ (C is the common atom of the two rings) on E_S and the angle θ. All the quantities in the range indicated vary in parallel but E_S increases more appreciably (than $^1J_{^{13}C-H}$ and θ) on passing from bicyclo[3,1,0]hexane to bicyclo-[2,1,0]pentane, but changes little on passing from the latter to bicyclo[1,1,0]butane. Nor is there a full correspondence between the changes in E_S and the changes in the $(C-C-C)_{av}$ angle. At the same time the constant $^1J_{^{13}C-H}$ varies linearly with the angle θ, a geometrical parameter of the bicyclic condensed molecule, which can be expressed by the equation

$$^1J_{^{13}C-H} = -176.0 + 3.123\,\theta\,. \qquad (14)$$

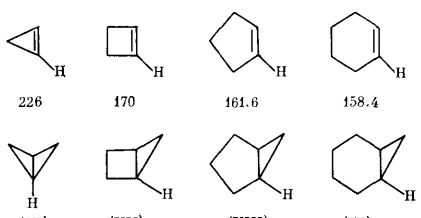
It is of interest to discover how $^1J_{^{13}C-H}$ changes when the double bond in the cycloalkene is replaced by a three-membered ring.

§The reference value of this angle, obtained[140] for butadiene, is 123.3(0.5)°.

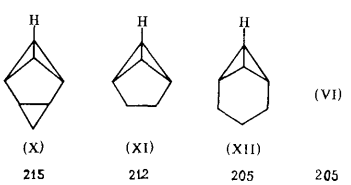
Table 7. The enthalpies of formation, strain energies, structural parameters, and SSCC of cyclopolyenes.

Molecule	$\Delta H^{\circ}_{f(L)}$	$\Delta H^{\circ}_{f(G)}$	E_s	Bonds	Valence angles	Dihedral angles	$^1J_{^{13}C-H}$	$^3J_{H-H}$
	25.16 (30)	31.26 (91)	4.8	1—2 1.509 (2) [133] 2—3 1.342 (3)	1—2—3 109.16 (10.0) 2—3—4 109.21 (10.0)	planar ring	170 [67]	5.06 [50, 51]
	17.52 (24)	25.41 (12)	4.2	1—2 1.350 (4) [134,135] 2—3 1.468 (14) 4—5 1.523 (16) 5—6 1.534 (20)	3—2—1 120.13 (0.6) 2—1—6 120.14 (0.5) 1—6—5 110.7	non-planar ring 1—2—3—4 16.3	163 [67]	9.42 [60]; 9.64 [49, 51]
	—	22.51 (22)	6.2	1—2 1.347 (6) [136] 2—3 1.450 (15) 4—5 1.509 (20) 5—6 1.522 (20) 1—H 1.092 (7)	1—2—3 129.1 (0.3) 2—1—7 129.1 (0.3)	non-planar ring deflective angle 5—6—7 / 4—5—7—6 63.9 (4.0)	—	8.9 [51]
	—	19.23	7.9	1—2 1.347 (5) [137] 2—3 1.475 (10) 4—5 1.509 (5) 5—6 1.542 (5)	1—2—3 129.0 (0.5) 4—5—6 117.2 (0.5) 5—6—7 105.9	non-planar ring 37.8 (1.0)	—	11.30 [51]
	34.44 (29)	43.69 (29)	3.7	1—2 1.356 (5) [138] 2—3 1.446 (7) 6—7 1.507 (7) 1—H 1.095 (10) 7—H 1.106 (10)	1—2—3 127.2 2—3—4 119.8 5—6—7 121.8 H—1—2 120 (2.0)	2—3—4—5 / 5—6—1—2 40.5 (20) 1—7—6 / 1—2—5—6 36.5 (20)	—	—
	60.83 (31)	71.13 (31)	16.9	1—2 1.340 (1) [139] 2—3 1.475 (1) C—H 1.100 (4)	1—2—3 126.1 (0.5)	1—6—5—2 / 2—3—4—5 43.1 (0.5)	155 [52]	—

Note. All the experimental values of ΔH°_f were taken from Pedley and Rylance[88] except $\Delta H^{\circ}_{f(G)}$ for cyclo-octa-1,3-diene which we calculated from the enthalpy of hydrogenation obtained in acetic acid solution at 25 °C.[7] We assume that the calculated value is reliable because the corrections disregarded in the calculation (the differences between the ΔH of solution and evaporation of cyclo-octa-1,3-diene and cyclo-octane) are in this case small. This follows from a comparison of the enthalpy of hydrogenation of its isomer cyclo-octa-1,5-diene obtained in acetic acid solution[7] with the value calculated from the enthalpies of combustion of cyclo-octa-1,5-diene (ΔH°_c = −1186.46 ± 0.31 kcal mol^{-1} [132]) and cyclo-octane[88].



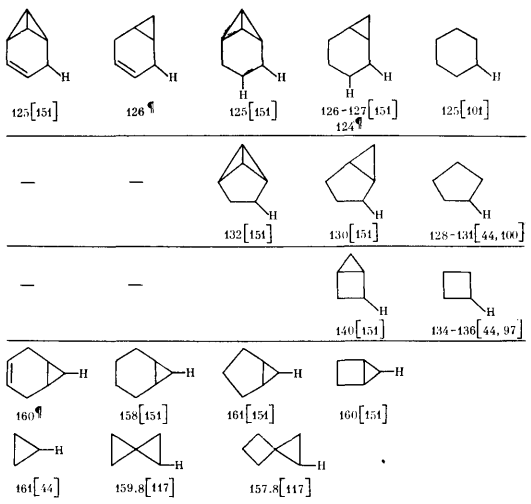
It is found that the bicyclic hydrocarbons (VI)–(IX) have higher constants than the corresponding cycloalkenes, the difference decreasing on passing from compound (VII) to (IX). The bicyclobutane (VI), for which $^1J_{^{13}C-H}$ is smaller than for cyclopropene, is an exception. The constants $^1J_{^{13}C-H}$ of the more complex polycyclic strained compounds (X)–(XII), whose composition includes the bicyclobutane fragment, are known.



Their geometrical and chemical parameters are unknown, but one can postulate that in the above series of compounds the strain energy E_S and the dihedral angles θ in the bicyclobutane fragment will diminish on passing from compound (X) to (VI), i.e. in conformity with the variation of the constant $^1J_{^{13}C-H}$.[151]

It is of interest to compare the values of $^1J_{^{13}C-H}$ for certain mono-, bi- and tri-cyclic hydrocarbons. Whereas the corresponding SSCC for the carbon atom common to both rings varies significantly with increase of the size of the larger ring and varies linearly with the dihedral angle θ (Fig.14), the constant $^1J_{^{13}C-H}$ for the nuclei of the "non-bridging" carbon atoms retains the specific value characteristic of the given ring and changes only slightly from compound to compound (the values of $^1J_{^{13}C-H}$ are given

under the formulae of the compounds below):



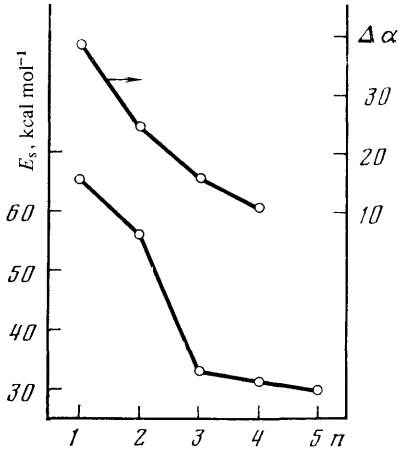
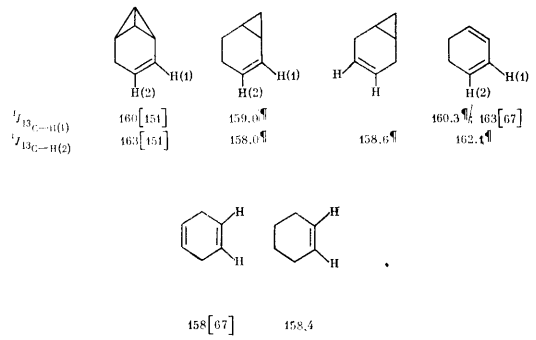


Figure 11. Variation of the strain energy E_S and $\Delta\alpha$ involving the tertiary carbon atom in bicyclo[n,1,0]alkanes: *1*) bicyclo[1,1,0]butane; *2*) bicyclo[2,1,0]pentane; *3*) bicyclo[3,1,0]hexane; *4*) bicyclo[4,1,0]heptane; *5*) bicyclo[5,1,0]octane.

It is also noteworthy that virtually identical values of $^1J^{13}C - H$ (involving the double bond) are characteristic of the unsaturated hydrocarbons presented below. The constants $^1J^{13}C - H(2)$ of tricycloheptene and the conjugated cyclohexadiene are somewhat larger:



5. Bicyclo[n,m,1]alkanes

(a) Correlation between the Strain Energy and Structural Parameters

The geometrical features of hydrocarbons of this class have been more thoroughly investigated than their thermochemistry†. We shall therefore carry out only a qualitative comparison of the geometrical parameters, using partly the calculated strain energies taken from Allinger et al.[17] and Engler et al.[18] (Table 9 and Fig.15).

Several hydrocarbons in this series have been reinvestigated but only in the case of norbornane were the errors of previous studies revealed by an electron diffraction investigation[163]. The situation is much less clear for bicyclo[1,1,1]pentane[158,159] and bicyclo[2,1,1]hexane[160,161]: for each of these compounds, Table 9 presents two sets of geometrical parameters. It is difficult to make a choice between them. The results for the bicyclo[2,1,1]hexane are striking: the author of a later study[161] claimed that his data were more accurate than the results of previous measurements[160]. Nevertheless his results[161] seem to be anomalous on the corresponding plots, deviating from the general relations. We therefore decided not to include them in the derivation of the correlation equations (16) and (17); they are shown in Fig.16 for comparison (see the filled circles).

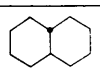
We shall consider how individual geometrical parameters vary, namely (a) the internuclear distances, (b) the valence angles, and (c) the dihedral angles.

(a) The most common geometrical element in the given series of hydrocarbons is the $-HC-CH_2-CH-$ bridge. The exact measurement of the C–C distances in the bridge involves a number of difficulties because the contributions of these distances to the overall diffraction patterns diminish significantly with increasing complexity of the molecule. We preferred to employ in this case the average distance $(C-C)_{av}$, which has been determined more accurately and which characterises the strain in the molecule as a whole. The variation of this parameter is illustrated graphically in Fig.15.

¶These data have been obtained by Yu.N.Luzikov in the Laboratory of NMR Spectroscopy of the Faculty of Chemistry of Moscow State University.

†Most thermochemical studies have been made on compounds of the norbornane series. Some compounds have been reinvestigated in different laboratories[155]. The results do not agree fully with one another and require further experimental confirmation.

Table 8. The enthalpies of formation, strain energies, structural parameters, and SSCC of the bridgehead C–H bond in bicyclo[*n*,1,0]alkanes.

Molecule	ΔH_f°(L)	ΔH_f°(G)	E_S	Bonds	Valence angles	Dihedral angles	$^1J_{13C-H}$
	46.30 (29)	51.91 (19)	65.6	1—3 1.497 (3) [143] 3—4 1.498 (4)	1—3—H 128°22′ (14′) H—C—H 115°34′ 1—2—3 59°58′	1—2—3 / 3—4—1 122°40′ (30′)	205 (2) [150—152] 202 [153]
	31.0 (34)	37.8 (40)	56.4	1—4 1.536 (1) [144] 2—3 1.565 (1) 1—2 1.528 (2) 1—5 1.507 (2)	5—1—H 121.2 (0.1) 4—1—H 128.6 (0.1)	1—5—4 / 1—2—3—4 67.3 (0.2)	178.1 (0.5) [78] 176 [151]
	1.22 (65)	9.15 (20)	32.7	1—6 1.515 (8) [145] 1—5 1.454 (9) 1—2, 2—3 1.543 (4) C—H 1.100 (6)	5—1—2 109.8 (0.4) 1—2—H 110.2 (1.1) 1—6—H 128.2 (3.7) 5—1—H 125.8 (6.4)	4—5—1—H 147.1 (10.1) 4—3—2 / 4—2—1—5 25.2 (2.8) 1—6—5 / 1—5—4—2 70.6 (1.1)	166 [151]
	28.8 (70)	—	—	1—5 1.521 (1) [146] 1—2 1.494 (10) 5—6 1.482 (6) 1—6 1.522 (7) 4—5 1.529 (15) 3—4 1.530 (15) 2—3 1.338 (10)	1—2—3 112.0 (1.0) 2—3—4 111.5 (1.0)	1—5—4 / 1—2—3—4 173.8 (1.5) 1—5—4 / 1—5—6 113.5 (1.0)	—
	−6.49 (30)	2.63 (31)	31.2	C—C 1.535 (8) [147] C—H 1.10 (1)	6—1—2 120 (1.0) 2—3—4 112 (1.5) 4—5—H 109 3—4—H 108 H—7—H 117	1—7—6 / 1—2—5—6 109 (2)	160 [151]
	−14.39 (26)	−3.97 (29)	29.5	—	—	—	—
	−17.48 (60)	−5.45 (60)	33.0	—	—	—	—
cis- 	−16.28 (42)	−6.31 (45)	27.2	*cis*-C–C$_{av}$ 1.536 (6) [148]	C—C—C (6-membered ring) 112.9 (4-membered ring) 88.9	torsional angle in 6-membered ring 48 torsional angle in 4-membered ring 157	—
				trans-C–C$_{av}$ 1.532 (5)	C—C—C (6-membered ring) 110.4 (4-membered ring) 87.3	torsional angle in 6-membered ring 57 torsional angle in 4-membered ring 145	
trans- 	−55.11 (21)	−43.52 (55)	−0.1	(C–C)$_{av}$ 1.530 (3) [149] C—H 1.112 (5)	C—C—C$_{av}$ 111.4 (0.4)	torsional angle 55.0 (0.5)	—

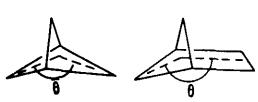
Note. The experimental values of ΔH_f° for the second, fourth, and fifth compounds were taken from Kozina[141] and those for the remaining compounds are from Pedley and Rylance[88].

(b) The valence angle ∠C–C–C (α) involving the bridging carbon atom in the symmetrical bicyclo[*m*,*n*,1]alkanes increases linearly on expansion of the rings on either side of the bridge, which is described by the following equation[5]:

$$\alpha = 0.836 + 18.282p^\circ , \qquad (15)$$

where $p = m + 3$. When this relation is recalculated in terms of the deviation from the standard angle 112.6°, another plot is obtained, which is also shown in Fig. 15.

(c) The geometrical parameters considered above vary almost linearly on expansion of the rings, while E_S varies non-linearly. The parameter which exhibits the best correlation with E_S proved to be the dihedral angle θ; it is shown below for bicyclo[1,1,1]pentane and bicyclo[2,1,1]-hexane.



The dependence of the angle on E_S is illustrated in Fig. 16 and is described by the equation

$$E_S = -1173.2 + 10.55\,\theta . \qquad (16)$$

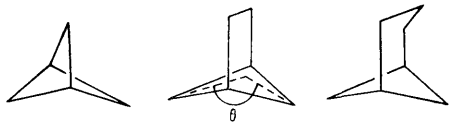
Bicyclo[*n*,1,1]alkanes, containing a four-membered fragment occupy a special place. The individual characteristics of these molecules are presented in Fig. 17; the data for cyclobutane have been included for comparison. Evidently, in contrast to the preceding case, the best correlation is observed between E_S and the ∠C–C–C (α) involving the secondary carbon atom in the four-membered ring (Fig. 18), which is described by the following empirical equation:

$$E_S = 430.5 - 4.550\,\alpha . \qquad (17)$$

(b) Correlation between Structural Parameters and SSCC

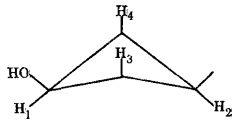
There are virtually no systematic data on the geometry and the SSCC for bridged hydrocarbons. The successive changes in the above parameters can be illustrated only in

relation to the three bicyclic hydrocarbons (XIII)–(XV):



(XIII) (XIV) (XV)

Each of these contains the cyclobutane fragment[53]. One of the characteristic parameters in the NMR spectra of compounds of this kind is the SSCC of the *exo, cis* protons via four σ-bonds, for which one can postulate a dependence on the dihedral angle θ in the four-membered ring (Table 9). The series of compounds considered can be logically completed by cyclobutane itself. The exact value of the constant $^4J_{H-H}$ of this compound is unknown but it is close to zero according to Meiboom and Snyder[167]. [$^4J_{H(1)-H(2)} = -0.01$ and $^4J_{H(3)-H(4)} = +0.01$ for cyclobutanol[168].]



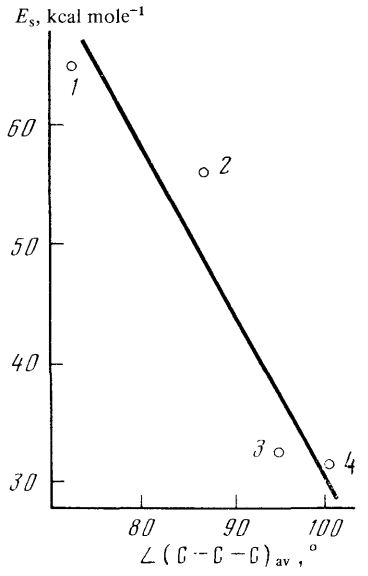


Figure 12. Variation of E_S with the average $(C-C-C)_{av}$ valence angle involving the tertiary carbon atom in bicyclo[n,1,0]alkanes: *1*)–*4*) see Fig.11; straight line—calculated by Eqn.(12).

Figs.19 and 20 (based on the data in Table 9) illustrate the changes in the constant $^4J_{H-H}$ and the angle θ for the hydrocarbons (XIII)–(XV) and cyclobutane as well as the linear relation between them, described by the equation

$$^4J_{H-H} = -0.285\,\theta + 44.026 \quad (18)$$

In determining the above correlation, bicyclo[1,1,0]butane should have been included, but two experimental values of the constant $^4J_{H-H}$, differing significantly from one another, are indicated in the literature: 10 Hz [86] and 5.9 Hz [150] (the latter agrees with theoretical values[152]). According to the relation established [Eqn.(18)], $^4J_{H-H}$ = 10 Hz should correspond to a dihedral angle of 122.4° for bicyclo[1,1,0]butane; however, when account is taken of the specific features of the structure of a system with two condensed three-membered rings, then the agreement with the data of Wiberg et al.[36] cannot apparently serve as a criterion of their validity.

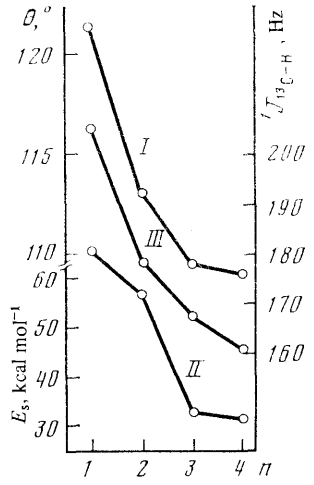


Figure 13. Variation of the dihedral angles θ (curve *I*), E_S (curve *II*), and $^1J_{^{13}C-H}$ (curve *III*) in bicyclo[n,1,0]-alkanes with the size of the larger ring: *1*)–*5*) see Fig.11.

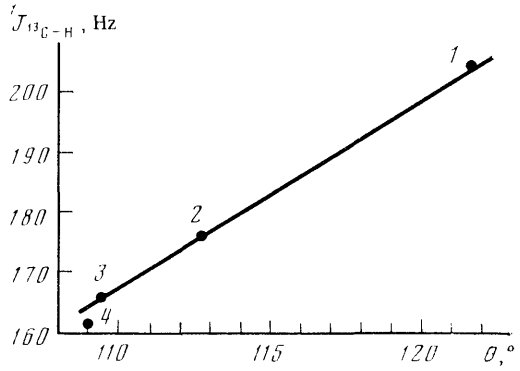
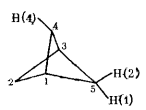
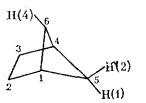
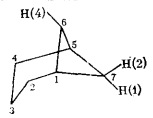
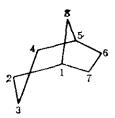
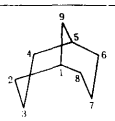
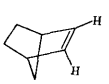
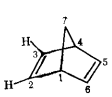
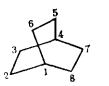
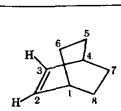


Figure 14. Variation of $^1J_{^{13}C-H}$ with θ for bicyclo[n,1,0]-alkanes: *1*)–*4*) see Fig.11; straight line—calculated by Eqn.(14).

It is possible to quote examples of successive changes in $^3J_{H-H}$ in a series of bridged hydrocarbons where five- or six-membered unsaturated rings are the repeating

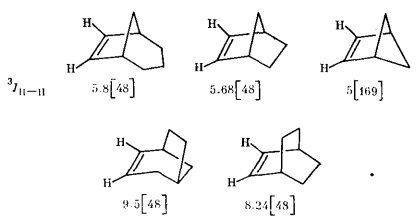
Table 9. The enthalpies of formation, strain energies, structural parameters, and SSCC of bicyclo[*m*,*n*,*k*]alkanes.

Molecule	$\Delta H^{\circ}_{f(L)}$	$\Delta H^{\circ}_{f(G)}$	E_s	Bonds	Valence angles	Dihedral angles	$^1J_{^{13}C-H}$	$^3J_{H-H}$	$^4J_{H-H}$	$^5J_{H-H}$
	—	—	(92.23) [17]*	C—C 1.557(2) [158] C—H 1.109(4) C—C 1.545(6) [159] C—H 1.100(10)	**1—2—3** 74.2(0.2) **H—C—H** 111.7(1.8) 1—2—3 73.3(1.0) H—C—H 103.9(5.0)	120 120	—	—3.0[53]	10[53]	—
	—	—	(41.21) [18]*	1—2 1.665(24) [160] 1—5 1.544(15) 2—3 1.513(15) C—H 1.112(5) 1—2 1.537(1) [161] 1—5 1.547(1) 2—3 1.537(1) C—H 1.098(4)	1—2—3 102.1 5—1—6 78.2 1—5—4 89.4 H—2—H 109.2(4.0) H—6—H 100.8(6.0) 1—2—3 100.4(0.4) 1—5—4 85.4(1.1) 5—1—6 83.3(1.2) 2—1—5 100.6(0.5) H—2—H 117.3(4.0) H—6—H 98.8(5.9)	1—5—4 / 1—6—4 125 1—5—4 / 1—6—4 129.5	—	—6.5—7.5 [53]	7—8 [53]	—
	—	—	(35.85) [18]*	1—2 1.511(15) [162] 2—3 1.534(30) 1—6 1.553(9) C—H 1.091(5)	**1—6—5** 87.1(1.0) 2—3—4 113.0(1.8) 1—2—3 108.7(1.1) 6—1—**2** 110.9(0.6) 6—1—7 **84.9**(1.4)	**1—6—5** / 1—7—5 137.5 2—3—4 / 4—5—1—2 143.0	—	—8.5—9.5 [53]	5.5—6 [53]	
	—22.01(52) [88]	—12.43(55) [88]	16.1	1—2 1.536(3) [163] 2—3 1.553(9) 1—7 1.558(9) C—H 1.112(2)	1—7—4 93.1(0.6) H—C—H 109.9(1.5)	1—6—5—4 / 1—2—3—4 113.1(0.6)	C(1)—H 141 [118] C(2)—H 130 C(7)—H 132	—	—	—
	—	—	(12.1)*	1—2 1.553(57) [170] 2—3 1.532(71) 1—8 1.501(54) 1—7 1.591(25) 6—7 1.544(60) C—H 1.109(6)	1—8—5 102.8(1.6) 2—3—4 109.6(2.5) H—C—H 101.2(6.0)	1—8—5 / 1—2—4—5 117.4(1.3) 2—3—4 / 1—2—4—5 41.1(2.8) 1—8—5 / 1—7—6—5 132.6(4.4)	— —	— —	— —	— —
	—42.6(20) [142]	—30.5(60) [142]	7.9	1—2 1.567(4) [5] 2—3 1.537(4) 1—9 1.476(5) C—H 1.116(4)	1—9—5 111.2(1.7) 2—3—4 111.5(1.4) H—C—H 106.3(2.4)	1—9—5 / 1—2—4—5 124.1(0.5) 1—2—4—5 / 2—3—4 141.6(1.6)	—	—	—	—
	9.89(33) [156]	19.14(35) [156]	19.8	—	—	—	165[82] 166.5[118]	—	—	5.6—5.9 [48,165, 166]
	—	58.0(60) [157]	27.2**	1—2 1.535(7) [162] 2—3 1.343(3) 1—7 1.573(14) C—H 1.123(14)	1—7—4 94.1(3.0) C—C—H 124(3) H—C—H 113(8)	1—2—3—4 / 1—6—5—4 115.6(2.2)	C(1)—H 172.5+ 172.8 [48,118, 165] C(7)—H 135 [118]			5.05 [165] 5.28 [48]
	—35.13(19) [88]	—23.66(22) [88]	9.8	1—2 1.538(15) [4] 2—3 1.552(29) C—H 1.107(9)	1—2—3 109.7(0.7) H—C—H 110.1(5.6)	—	—	—	—	—
	—5.57(17) [88]	4.90(19) [88]	10.5	1—2 1.509(15) [164] 2—3 1.341(8) 1—8 1.549(8) 7—8	1—2—3 114.2(0.6) 2—3—H 122.4(6.0) H—C—H 109.2(4.0)	1—2—3—4 / 1—6—5—4 121.2(2.1)	162.8 [48]	—	—	8.24 [48]

*Calculated data.

**Estimated using the difference between the heats of hydrogenation of norbornene and norborna-2,5-diene.

elements[48]:



The values of E_S for both series increase from left to right, i.e. in conformity with the decrease of the SSCC of the vicinal protons. Probably $\angle C = C-C$ varies in the same sequence (analogously to the variation of the corresponding parameters for cycloalkenes).

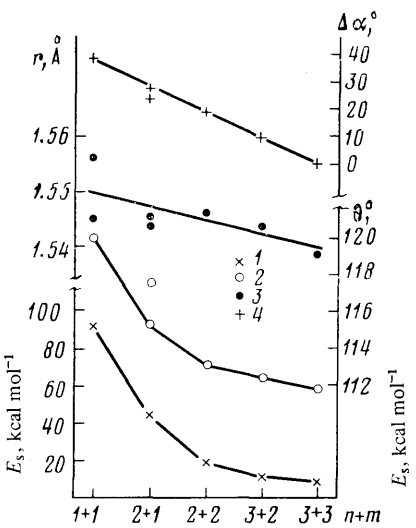


Figure 15. Variation of the strain energy E_S (*1*), the average $(C-C)_{av}$ internuclear distance (r) (*3*), the difference $\Delta\alpha = 112.6° - \alpha$ (α is the C–C–C angle in the bridge) (*4*), and the dihedral angle θ (*2*) in bicyclo[n,m,1]alkanes with the size of the ring; bicyclo[1,1,1]pentane and bicyclo-[2,1,0]hexane were investigated twice.

III. CONCLUSION

The most general comment which can be made on the basis of the data considered concerns Eqn.(1). The experimental data presented in Section II show that in fact two separate relations exist:

$$E_s\text{-molecular geometry and SSCC-molecular geometry.} \qquad (1')$$

They cannot be combined in terms of geometrical data because in most cases different geometrical parameters are involved in the quantitative relations.

The only deviation from this rule arises in the case of cycloalkenes [see Eqns.(8), (10), and (11)]. However, one should note that, despite the absence of quantitative relations, the SSCC vary in parallel with E_S. In those cases where deviations are observed from such parallel variation [for example in the cyclo-octane–cyclononane (Fig.5) and cyclohexene–cycloheptene (Fig.9) transitions], an experimental test of the corresponding parameters would be desirable.

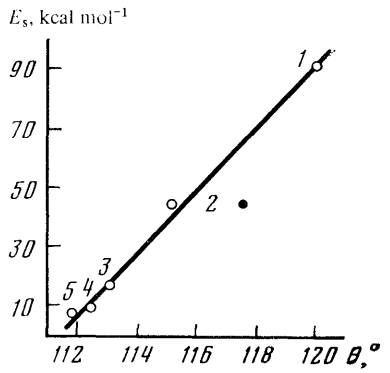


Figure 16. Variation of the strain energy with θ for different bicyclic hydrocarbons: *1*) bicyclo[1,1,1]pentane: *2*) bicyclo[2,2,1]hexane; *3*) bicyclo[2,2,1]heptane; *4*) bicyclo[3,2,1]octane; *5*) bicyclo[3,3,1]nonane; straight line—calculated by Eqn.(16); filled circle—Chiang's data[161].

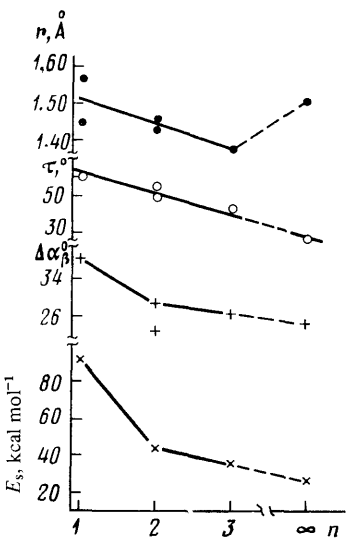


Figure 17. Variation of the strain energy E_S, the average $(C-C)_{av}$ internuclear distance (r), the dihedral angle in the four-membered fragment γ, and the difference $\Delta\alpha = 112.6° - \alpha$ (α is the C–C–C valence angle at the secondary carbon atom in the four-membered fragment) in bicyclo[n,1,1]-alkanes and cyclobutane (the convention is adopted that for this compound $n = \infty$).

For each series of the cyclic hydrocarbons considered, there is a definite correlation between the SSCC and the angular parameters of the molecule; no dependence on the

internuclear distances has been observed. One can postulate on the basis of the available (limited) data, that such correlations between the SSCC and the angular parameters of the molecule can be found also in other series of hydrocarbons when the amount of the relevant experimental data is sufficient.

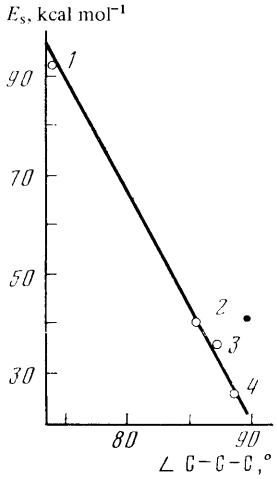


Figure 18. Variation of the strain energy with the C–C–C valence angle in the four-membered fragment in different bicyclic hydrocarbons: *1*) bicyclo[1,1,1]pentane; *2*) bicyclo[2,1,1]hexane; *3*) bicyclo[3,1,1]heptane; *4*) cyclobutane; straight line—calculated by Eqn.(17); filled circle—Chiang's data[161].

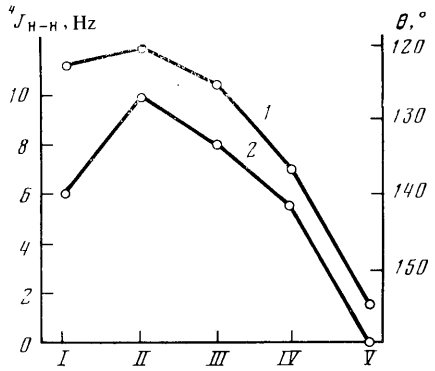


Figure 19. Variation of the dihedral angle θ in the four-membered fragment (curve *1*) and $^4J_{H-H}$ (curve *2*) in bicyclo[*n*.1.1]alkanes (*II–IV*), bicyclo[1,1,0]butane (*I*), and cyclobutane (*V*).

If the variation of E_S in the series of compounds considered as a function of the number of carbon atoms *n* is followed {for bicyclo[*n*,1,0]alkanes, *n* is the number of carbon atoms in the larger ring and for symmetrical bridged hydrocarbons it is the number of carbon atoms in each ring} (Fig.21), it is found that the nature of the variation of E_S in the series of bicyclo[*n*,1,0]alkanes and cycloalka-1,3-dienes is approximately the same, the values of E_S for rings with *n* between 5 and 8 being similar. In each series of compounds hydrocarbons containing six-membered rings have the smallest values of E_S regardless of which structural parameters (bond length, valence or dihedral angles) are mainly used to determine E_S. Bicyclo[*n*,1,0]alkanes, where the minimum is displaced to the hydrocarbon with the larger seven-membered ring, are an exception, but in this case there are grounds for recommending the redetermined values of ΔH_f° for bicyclo[5,1,0]octane#.

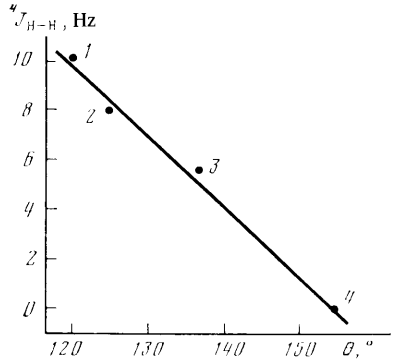


Figure 20. Variation of $^4J_{H-H}$ with θ: *1*)–*4*) see Fig.18.

The introduction of a correction for the contribution of the energy $p\Delta V$ to E_S does not alter the nature of the curves, which are merely displaced by 0.6 or 1.2 kcal mol^{-1}.

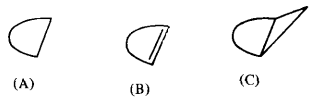
The strain energies E_S of cyclohexane, cyclohexene, cyclohexa-1,3-diene, and bicyclo[2,2,2]octane per six-membered ring are −0.2, 1.1, 4.2, and 4.9 kcal mol^{-1} respectively. The conformation of the six-membered ring in these hydrocarbons varies as follows: chair → half-chair → flattened half-chair → boat. However, one should note that the above values of E_S cannot be used to estimate the energy of the chair → half-chair → boat conformational transition for a six-membered ring, since the values of E_S reflect the overall strain energy and not the conformational energy.

We examined above how E_S is related explicitly to the geometrical parameters and the SSCC and how it varies in a specific series of compounds with the number of carbon atoms. It is also of interest to trace the variation of the

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#The value of ΔH_f° for bicyclo[4,1,0]heptane quoted by Dashevskii[16], whose results we have employed, differ from the other literature values by 2.3 kcal mol^{-1}. In this connection, the enthalpy of combustion of bicyclo[5,1,0]-octane has been redetermined. The following values (in kcal mol^{-1}) have been obtained at 298 K: $\Delta H_{c(L)}^\circ$ = −1218.80 ± 0.45; $\Delta H_{f(L)}^\circ$ = −11.82 ± 0.47; $\Delta H_{f(G)}^\circ$ = −1.42 ± 0.51; E_S = 32.1. This value of E_S is presented in Fig.21 (the experimental work has been carried out by L.P.Timofeeva).

relative values of E_S characterising the transition from cycloalkanes (A) to the corresponding cycloalkenes (B) and the bicyclo[n,1,0]alkanes (C):



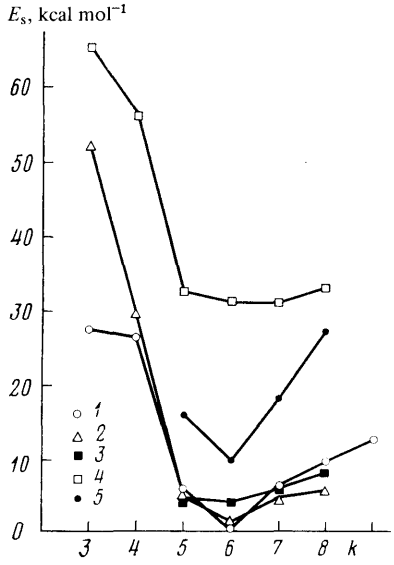
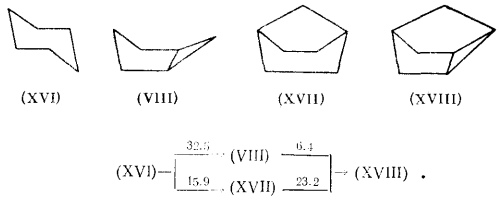


Figure 21. Variation of E_S in the series of cycloalkanes (*1*), cycloalkenes (*2*), cycloalkadienes (*3*), bicyclo[n,1,0]alkanes (*4*), and symmetrical bridged bicycloalkanes (*5*) with the number of carbon atoms in the ring for (*1*), (*2*), and (*3*), with the number of carbon atoms in the larger ring for (*4*), and with the number of carbon atoms in one of the rings for (*5*).

Fig. 21 presents the variation of E_S for each of these series and Fig. 22 presents the differences $\Delta E_S^{(1)} = E_S(B) - E_S(A)$ and $\Delta E_S^{(2)} = E_S(C) - E_S(A)$. Each of the quantities $\Delta E_S^{(1)}$ or $\Delta E_S^{(2)}$ considered separately corresponds to the additional strain in the cycloalkane molecule which appears as a consequence of the introduction of a double bond or a three-membered ring respectively. Comparison of the two sequences of the values of $\Delta E_S^{(1)}$ and $\Delta E_S^{(2)}$ demonstrates the approximately identical nature of their variations in series (B) and (C). It is known[145] that there are analogies between the conformations of the carbon ring in these hydrocarbons determined by the absence of internal rotation relative to the double bonds in series (B) or the common bond in the bicyclic systems (C).

It is of interest to trace the changes in E_S on passing from monocyclic to bicyclic and tricyclic hydrocarbons in the series below:



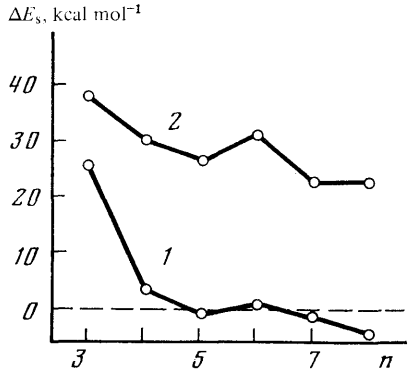


Figure 22. Variation of the differences $\Delta E_S^{(1)} = E_S(B) - E_S(A)$ (curve *1*) and $\Delta E_S^{(2)} = E_S(C) - E_S(A)$ (curve *2*).

(Unfortunately such examples are limited owing to the insufficient amount of experimental data.) The greatest change in E_S corresponds to the introduction of a three-membered ring into the system. The methylene bridge linking the first and fourth carbon atoms causes smaller changes in E_S, particularly when the trimethylene ring is already in the molecule. The overall change in E_S on passing from cyclohexane to the nortricyclene (XVIII) via compound (VIII) or (XIV) is virtually the same, which confirms the validity of the quantities used in the calculations.

On the basis of the empirical equations relating E_S to different geometrical parameters which have been derived, a slightly different meaning can be given to the reference values of r_0 and α_0. We recall that we adopted these values from data for the molecules with the minimum E_S, associated with the given geometrical parameter. For example, saturated hydrocarbons ranging from methane to n-heptane, *cis*-butene, and isobutane have been used as standards. With the aid of the above correlation equations, we can now carry out a kind of test of these values by determining them from the condition for the equality of E_S to zero. The values obtained from the empirical equations (we shall designate them by r_0' and α_0' respectively) can be regarded as generalised constants satisfying sets of molecules and related directly to E_S.

The values of r_0 and α_0 used previously are compared below with their analogues r_0' and α_0' calculated from empirical equations (4), (8), and (9):

C–C bond	$r_0 = 1.533$ (1) Å	$r_0 = 1.537$ Å	calc. by Eqn.(4),
C=C–C angle	$\alpha_0 = 125.4$ (0.4)°	$\alpha_0' = 124.5°$	calc. by Eqn.(8),
C–C–C angle	$\alpha_0 = 112.6$ (0.1)°	$\alpha_0' = 112.5°$	calc. by Eqn.(9).

It is noteworthy that the reference values of the angular parameters which we used above and the values calculated by Eqns.(8) and (9) are very similar. Evidently this shows that the selected acyclic systems are indeed free from angular strain, which arises in cyclo-olefins and is described by Eqns.(8) and (9). The discrepancy of 0.004 Å between r_0 and r_0' may not be fortuitous and may have a perfectly definite significance, because $r_0' = 1.537$ Å is virtually identical with the C–C distance in cyclohexane (1.536 Å), for which E_S is close to zero. The increase in the length of the C–C bond in cyclohexane may arise as a consequence of inevitable *gauche*-interactions[13]. Similar *gauche*-interactions in acyclic systems with a short-carbon chain are much less appreciable[39].

Analogous calculations using other empirical equations do not yield interesting results, which may be due to the specific features of the geometrical parameters considered or the inadequate number of experimental data [for example, the average angle $(C–C–C)_{av}$ in Eqn.(12)].

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The Electronic and Steric Effects in Heterolytic Intramolecular Cyclisation Reactions

R.Valters

Data concerning the influence of the electronic and steric effects of substituents as well as the structure of the connecting units on the rate and equilibrium constants for cyclisation reactions, occurring as intramolecular nucleophilic addition to a trigonal carbon atom, are examined. The general characteristics permitting the prediction of the ease of ring closure and the stability of the heterocycles are specified.
The bibliography includes 166 references.

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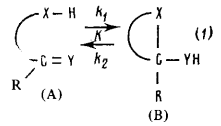
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I. INTRODUCTION

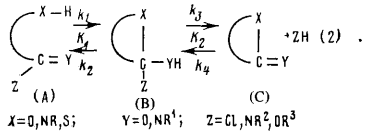
The assessment of the influence of structural factors on intramolecular cyclisation reactions makes it possible to predict the ease of formation and the stability of heterocycles[1-3]. Factors promoting ring closure act similarly in the recyclisation reactions of heterocycles[4], in intramolecular catalysis[5-10], in the migration of acyl and other groups[8,10-12], and in other reactions which proceed with formation of cyclic transition states or cyclic intermediates. Studies of the mechanisms of enzymatic reactions[8,9,13-15], of the formation of chelates[16], and of the intramolecular hydrogen bond[17-19] are closely related to the problem of the influence of structural factors on intramolecular cyclisation.

The aim of the present review is to examine the influence of the electronic and steric effects of substituents at the reacting groups and the structure of the unit connecting them (the carrier system) on the relative stabilities of the heterocycles formed (represented by $\lg K$, where K is the ring–chain equilibrium constant) or on the ease of their formation (represented by $\lg k$, where k is the rate constant for the cyclisation reaction).

We shall confine ourselves to the consideration of the intramolecular nucleophilic reactions involving the addition of the O–H, N–H, and S–H groups to the multiple polar bonds C=Y [reactions (1)] occurring with subsequent elimination [reactions (2)] or without it, i.e. with retention or cleavage of the tetrahedral intermediate; there is yet another limitation, i.e. only the closure of the so-called[2] normal, i.e. five-membered, six-membered, and seven-membered, heterocycles will be considered†. The molecular fragment which constitutes the carrier system for the groups reacting with one another is designated by a half-circle in Eqns.(1) and (2).



(1)



(2)

This choice makes it possible to employ the accumulated data on the ring–chain isomerism of organic compounds[20-23]; it is dictated primarily by the availability of quantitative literature data precisely for such reactions.

In reaction (1) the thermodynamic stability of the ring will be characterised by the ring–chain equilibrium constant K or the free energy difference ΔG, which is proportional to the logarithm of K. It is most rational to examine the influence of the relevant structural factors precisely on the equilibrium constant K. However, one must then take into account the fact that small changes in structure very frequently displace the system from the state of tautomeric equilibrium[12,23] and the possibility of employing the equilibrium constant for comparative purposes is lost. The use of the enthalpy and entropy components (ΔH and ΔS) of the free energy difference is limited by the comparatively small amount of experimental data. The use of ΔH and ΔS involves a number of uncertainties which are difficult to overcome and which have been examined by Jencks[9] (p.246). Among these, the impossibility of applying corrections for solvation effects is most important for reactions in solutions.

The energetic aspect of intramolecular reactions with separate analysis of the enthalpy and entropy contributions and their comparison with intermolecular reactions have been described in a review[24]. It is easy to show that the estimation of the individual components of the difference between the potential energies of the open-chain and cyclic structures, which are due to changes in bond lengths, the deformation of valence angles, the non-bonding and electrostatic interactions, steric strain, solvation, and the formation of hydrogen bonds, is difficult to achieve experimentally.

†The influence of structural factors on cyclisation reactions with formation of large rings has been examined in a recently published review: G.Illuminati and L.Mandolini, Acc.Chem.Res., 1981, **14**, 95.

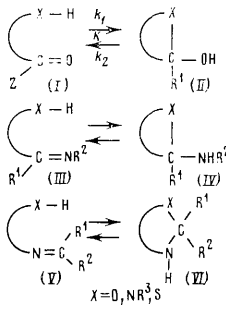
The use of the cyclisation rate constant k_1 for the estimation of the ease of formation of the ring is associated with another type of uncertainty. The transformation (A) → (B) [Scheme (1)] consists of three stages: the abstraction of a proton from the group X–H, the formation of the X–C bond, and the addition of a proton to Y. The sequence of these stages is determined by the acidity of the groups X–H and Y–H and also by the protolytic properties of the medium and is not the same for different systems[23]. The ease of formation of the ring is characterised by the constant k_1 (or the corresponding activation energy $\Delta G^{\neq}$) only when the ring closure stage, i.e. the formation of the X–C bond, is slowest and the transition state has a cyclic structure. However, this is not always the case, because it has been shown experimentally for certain ring–chain tautomeric systems that the rate is limited by the proton transfer stage[25–27].

The suitability of thermodynamic and kinetic characteristics of the second group of reactions [reactions (2)] for the estimation of the stability and ease of formation of heterocycles is limited by the presence of the stage involving the cleavage of the tetrahedral intermediate. The equilibrium (B) ⇌ (C) is usually displaced to the right, but it is necessary to take into account the fact that the equilibrium constant $K = [B]/[A] = k_1/k_2$ and k_2 can be determined experimentally only by an indirect method.

The employment of the kinetically determined rate constant for the transformation (A) → (B) for our purposes is also correct (when account is taken of the considerations presented above) only when $k_1 < k_3$.

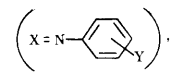
II. ELECTRONIC EFFECTS OF SUBSTITUENTS AT THE REACTING GROUPS

Inspection of a large number of ring–chain equilibrium systems of the type (I) ⇌ (II), (III) ⇌ (IV), and (V) ⇌ (VI) [23] permits the conclusion that the stability of the cyclic form, produced as a result of the intramolecular nucleophilic addition of the group X–H to a polar multiple bond, increases in the sequence of atoms X = O < N < S (naturally, other structural conditions being equal or similar).



This sequence agrees with the equilibrium constants for intermolecular reactions involving addition to the C=O bond[28] and can be accounted for both by the increase of the nucleophilicity of the atom X and by the smaller strain energy[24] in sulphur-containing heterocycles compared with the oxygen- and nitrogen-containing heterocycles.

The influence of the nucleophilicity of the atom X on the stability of the cyclic isomer can be traced in the series of amino-derivatives with different substituents at the nitrogen atom. Thus the introduction of electron-donating substituents Y into the phenyl group at the nitrogen atom

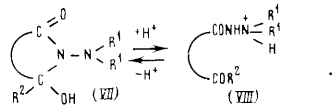


shifts the equilibrium towards the cyclic form, while electron-accepting substituents shift the equilibrium in the opposite direction[29,30]. The foregoing is confirmed by the negative value of the constant ρ,[30] obtained from the correlation between the ring–chain equilibrium constants for *N*-arylamides of 3,3-dimethyl-levulinic acid and the polar constants of the substituents Y (Table 1).

N-Methylated derivatives (X = NCH_3) almost always exhibit a greater tendency towards cyclisation than their analogues unsubstituted at the nitrogen atom (X = NH).[38–48] Several exceptions can be explained[44–46] by the steric influence of the methyl group, which destabilises the cyclic structure. As the length and degree of branching of the alkyl substituent at the nitrogen atom increase, its electronic influence cannot be estimated, because the steric effects are much stronger.

The cyclic structure is also destabilised by the decrease of the nucleophilicity of the nitrogen atom as a result of the introduction of aryl or acyl substituents at this atom[23].

The protonation of the dialkylamino-group in the cyclic isomer of the *N,N*-dialkylhydrazide of a 3-acylcarboxylic acid proceeds with ring opening [(VII) → (VIII)], while deprotonation is accompanied by the reverse process[47,48]. This phenomenon can be explained by the influence of the strong $-I$ effect of the substituent $N^+HR_2^1$, which reduces the nucleophilicity of the second nitrogen atom.



The higher ring–chain equilibrium constants in solutions for 2-acylmercaptoperimidines compared with 2-acylmercaptobenzimidazoles have been explained[49] by the greater basicity of the perimidine nitrogen atom compared with the benzimidazole nitrogen atom.

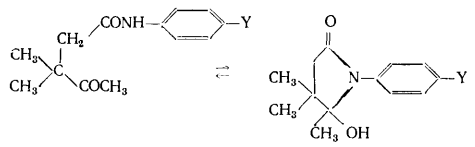
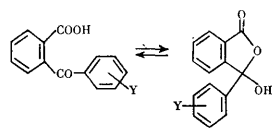
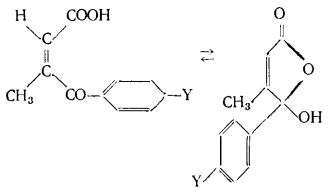
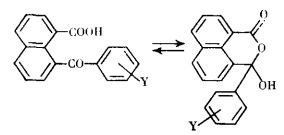
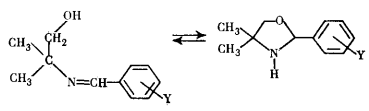
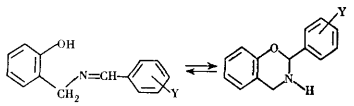
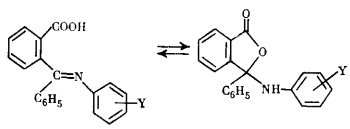
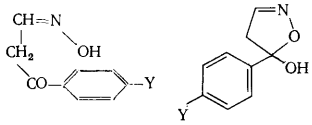
In the series of 3- and 4-acylcarboxylic acid [(I) ⇌ (II), X = COO] it is easy to trace the influence of the structure of the substituent on the ring–chain equilibrium constants. A pronounced shift of the equilibrium towards the cyclic form in the series of substituents aryl < alkyl < H is observed[21,23]. The enhanced stability of the open-chain isomers of aroylcarboxylic acids is caused not only by the reduced electrophilicity of the carbon atom of the group ArCO but also by the gain of the conjugation energy.

For tautomeric systems producing the cyclic form as a result of intramolecular addition to the C=N bond, the pattern of the influence of the electronic effect of substituents at this bond is more complex[50].

For hydroxyaldehyde imines [(III) ⇌ (IV), X = O, R^1 = H], the equilibrium is much more displaced towards the cyclic form than for hydroxyketone imines [(III) ⇌ (IV), X = O, $R^1 = CH_3$].[51] Similarly the *N*-(2-hydroxyalkyl)hydrazones of aldehydes show a greater tendency towards cyclisation compared with the *N*-hydroxyalkylhydrazones of ketones[50,52]. However, in this case the electronic effect of the alkyl group, which reduces the electrophilicity of the carbon atom in the C=N bond, is overlapped by the stronger steric effect of the alkyl substituent, which destabilises the cyclic structure[50–52].

The opposite effect has been observed[53] in the series of *N*-(2-mercaptoalkyl)hydrazones of aromatic aldehydes: on passing from a benzaldehyde derivative to an acetophenone derivative, the ring–chain equilibrium shifts towards the

Table 1. Examples of the linear correlation of the ring–chain tautomeric equilibrium constants $K = [B]/[A]$ and the polar constants of the substituents Y in the benzene ring at the reaction centre.

Ring-chain equilibrium (A) ⇄ (B)	Solvent	Method of determination of K	lg K/K_0	n	r	References
	50% aqueous pyridine	^{1}H NMR	$-1.38\,\sigma^+$ $-1.85\,\sigma$ $-1.45\,\sigma^-$	8	1.96 0.93 0.94	[30]
	$MeNO_2$ MeCN dioxan $CHCl_3$	i.r.* i.r. i.r. i.r.	$0.87\,\sigma$ $0.60\,\sigma$ $0.54\,\sigma$ $1.15\,\sigma$	9	— — — —	[31]
	dioxan	i.r.	$0.374\,\sigma_I + 1.885\,\sigma_R^0$	6	0.990	[32]
	dioxan	i.r.	$1.286\sigma_I + 2.918^0_R$	8	0.970	[33]
	CCl_4	^{1}H NMR	$0.856\,\sigma$ $0.543\,\sigma^+$	8	0.973 0.999	[34]
	$CDCl_3$	^{1}H NMR	$0.738\,\sigma$ $0.680\,\sigma^+$	5	0.993 0.999	[34,35]
	*dioxan*	u.v.**	$0.58\,\sigma$ $0.35\,\sigma^+$	7	0.94 0.97	[36]
	C_5D_5N	^{1}H NMR	$1.26\,\sigma^+$ $1.41\,\sigma_I + 1.26\,\sigma_R^+$	9	0.993	[37]

Note. K_0 is the ring–chain equilibrium constant for the unsubstituted derivative (Y = H), K the constants for substituted derivatives, n the number of compounds with different substituents Y, and r the correlation coefficient. The signs of the constants ρ are quoted in accordance with the condition $K = [B]/[A]$. Sheiman et al.[30] and Paukstelis and Lambing[34] calculated the equilibrium constants from the formula $K = [A]/[B]$.

*Infrared spectroscopy. ** Ultraviolet spectroscopy.

cyclic form, which has been explained by the influence of the breakdown of the conjugation $\rangle N-N=\overset{|}{C}-Ar$ in the open-chain isomer after the introduction of the methyl group.

The *N*-(2-hydroxybenzyl)imines of aromatic aldehydes exhibit a smaller tendency towards cyclisation than the corresponding derivatives of acetone or cyclohexanone[35] owing to the gain in the conjugation energy in the open-chain isomer.

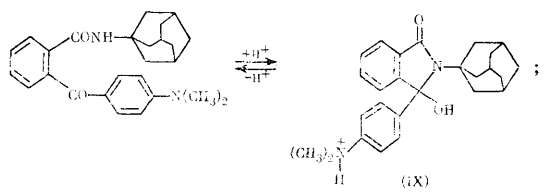
An increased stability of the cyclic form has been observed in the *N*-arylimines of 5-hydroxypentanal compared with the *N*-alkylimines[51,54,55]. The authors explain this remarkable effect by the energy gain in the $p-\pi$ conjugation of the unshared electron pair of the nitrogen atom with the arene ring in the cyclic isomer compared with the $\pi-\pi$ conjugation,

which is disrupted, according to the authors, by the non-coplanarity of the C=N–Ar system in the open-chain isomer.

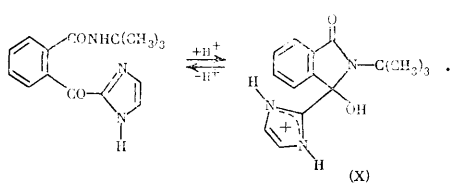
The introduction of an acyl group at the imine nitrogen atom in the imines of 2-benzoylbenzenesulphonamides stabilises the cyclic structure of 3-acylamino-3-phenylbenzoisothiazoline 1,1-dioxides[56]. The introduction of electron-accepting substituents Y in the phenyl groups of the C=O or C=N bonds [R^1 and R^2 in compounds (I)–(VI)] as a rule shifts the equilibrium towards the cyclic form, while electron-donating substituents act in the opposite direction. This conclusion confirms the examples of the linear correlation of the ring–chain tautomeric equilibrium constants for aroylcarboxylic acids and their *N*-arylimines, *N*-(2-hydroxybenzyl)- and *N*-(2-hydroxyalkyl)aldimines, and 3-aryl-1-hydroxyimino-3-propanones with the polar constants of the substituents Y ($\rho > 0$), which are presented in Table 1.

In addition, for certain systems, for example, for *N*-t-alkyl-2-aroylbenzamides, the introduction of electron-accepting substituents in the aroyl group made it possible to obtain cyclic isomers of compounds which did not undergo cyclisation in the absence of such substituents[57,58]. The rate constants for the interconversions of the isomers then increase and the equilibrium shifts towards the cyclic form[59].

An interesting example of the stabilisation of the cyclic form of *N*-t-alkyl-2-(4-dimethylaminobenzoyl)benzamides (IX) and 2-(2-imidazoylcarbonyl)benzamides (X) by the protonation of the dimethylamino-group or the imidazole ring has recently been observed[60–62].



(IX)

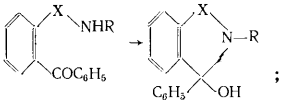


(X)

The protonation of the nitrogen-containing substituent increases its $-I$ effect, which enhances the electrophilic properties of the carbon atom of the C=O group and displaces the equilibrium towards the cyclic form. Deprotonation is accompanied by the reverse process.

Numerous qualitative and quantitative data[20–23] confirm the following general rule: the influence of the electronic effects of substituents on the relative stabilities of cyclic isomers formed as a result of the intramolecular nucleophilic addition of the group X = H to the polar multiple bonds C=O, C=N, etc. can be predicted by estimating the influence of these substituents respectively on the nucleophilic and electrophilic properties of the atoms between which the bond is formed on ring closure. As the nucleophilic properties of the atom X are enhanced and (or) with increase of the electrophilicity of the carbon atom in the groups C=O, C=N, etc., the equilibrium shifts towards the cyclic form.

This rule applies not only to the substituents R^1, R^2, and R^3 in compounds (I)–(VI) but also to the electronic influence of the structure of the connecting unit and the substituents incorporated in this unit. Thus it has been shown that 2-benzoylbenzenesulphinamides are capable of intramolecular cyclisation [(XI) ⇌ (XII), X = SO],[63] whereas the analogous reaction for 2-benzoylbenzenesulphonamides (XI, X = SO_2) is not feasible[64]. This phenomenon can be explained by the reduction of the nucleophilicity of the nitrogen atom on passing from the sulphinamide to the sulphonamide group.



(XI) (XII)

X = SO, SO_2 .

However, the estimation of the electronic influence of the structure of the connecting unit on the reacting groups is associated with difficulties due to the overlap of the electronic effects with the steric effects, which alter the geometry of the mutual approach of the reacting groups.

The influence of the electronic effects of the substituents on the ring–chain equilibrium constants can be effectively predicted in conformity with the principle of the linearity of the variation of the free energies in those cases where the substituents are introduced into aryl groups at the reaction centres.

When the substituents R^1, R^2, or R^3 in compounds (I)–(VI) are varied in the sequence H, alkyl, aryl, their electronic influence is much more difficult to estimate, because it is then necessary to take into account also their steric effects, the gain in the stabilisation energy of the corresponding isomers as a result of the conjugation of the C=O and C=N bonds or the *p* electrons of the nitrogen atom with the aryl substituents, the stabilisation of the individual isomers as a result of the formation of intramolecular and intermolecular hydrogen bonds, or various solvation effects.

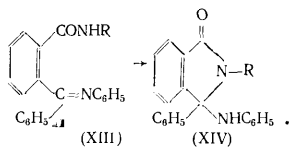
An estimate[23] of the thermodynamic stabilities of cyclic isomers from the changes in the nucleophilic and electrophilic properties of the reaction centres aroused objections[65], because a kinetic characteristic was used to estimate thermodynamic quantities. Although the stabilities of the corresponding cyclic isomers are usually satisfactorily correlated with the O < N < S nucleophilicity series in relation to the electrophilic carbon, one may agree that, in comparing different atoms X acting as nucleophilic centres, it is necessary to take into account also factors such as the different strains in the rings formed, the different capacities for the formation of hydrogen bonds, etc. However, under the influence of substituents, the difference between the free energies of the isomers varies in proportion to the difference between the free energies of activation, i.e. the polar constants of the substituents are correlated both with the equilibrium constants and with the reaction rate constants[66].

In other words, the changes in the structures of the carbonyl compounds are reflected similarly in the rates and equilibria of non-catalysed reactions involving addition to the carbonyl group, because both the transition state and the final product are destabilised by electron-accepting substituents to a smaller extent than the initial carbonyl compound[28].

III. STERIC EFFECTS OF SUBSTITUENTS AT THE REACTING GROUPS

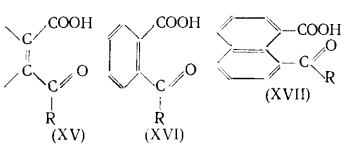
In order to estimate the steric influence of substituents at the reacting groups on the relative stabilities of cyclic isomers, the influence of the substituents on the possibility of the optimum intramolecular mutual approach of the reaction centres is usually considered. A more profound approach involves the calculation or empirical estimation of the difference between the energies of the non-bonding interactions between the substituent and the remainder of the molecule in the open-chain and cyclic isomers.

An increase in the length and branching of the alkyl substituent at the nitrogen atom in aminocarbonyl compounds [(I) ⇌ (II), X = NMe > NEt > NPr-iso > NBu-t] destabilises the cyclic structure. There exist examples of such influence on the ring–chain isomerism of *N*-monosubstituted amides of acylcarboxylic acids[21,23,56,67–69], *N*-alkyl-*N'*-(3-oxoalkyl)-thioureas[70], *S*-(2-oxoalkyl)dithiocarbamates[71], and other compounds[23]. Similar features have also been observed for reactions involving intramolecular addition to the C=N bond. Increasingly severe conditions are required for the isomerisation (XIII) → (XIV) in the presence of the series of substituents R = Pr, $PhCH_2$, iso-Pr, or t-Bu at the nitrogen atom[72]. The reverse reaction—the thermal isomerisation of the aminolactam [(XIV) → (XIII)]—has been achieved for the first time in the case of *N*-t-butylamide[73,74]:



Branching of the alkyl substituent at the keto-group [R^1 in formulae (I) and (II)] in different systems has the opposite influence on the stability of the cyclic form:

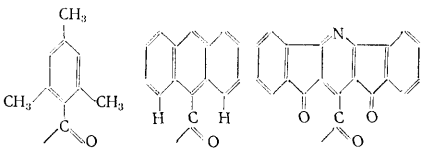
(1) If the connecting unit contains a double bond or an aromatic ring conjugated with the keto-group, as happens in *cis*-3-acylacrylic acids (XV),[75] 2-acylbenzoic acids (XVI),[76] and 8-acylnaphthoic acids (XVII),[33] then an increase in the bulk of the alkyl substituent R in the sequence Me < Et < iso-Pr < t-Bu shifts the equilibrium (I) ⇌ (II) (X = COO) towards the cyclic form:



With increase of the bulk of R, the keto-group "unscrews itself" from the plane of the double bond or the aromatic ring and assumes the conformation most suitable for intramolecular addition; furthermore, the electrophilicity of the carbonyl carbon atom increases owing to the decrease of the effect of conjugation as coplanarity breaks down. All these factors destabilise the open-chain structure. In the series of 8-acylnaphthoic acids (XVII)[33] the ring–chain equilibrium constants are satisfactorily correlated with the Taft steric substituent constants E_S [$\lg(K/K_0) = -0.60\,E_S$, $r = 0.977$].

(2) If the connecting unit forms a conformationally mobile chain, the opposite effect is observed: an increase in the bulk of the substituent R destabilises the cyclic structure. Thus, on branching of the substituent, the content of the cyclic form decreases in the series of *S*-(2-oxoalkyl)dithiocarbamates[71], 2-acylmethylmercaptobenzimidazoles[49,77], 2-acylmethylmercaptoperimidines[49], and 1-(2-oxoalkyl)-3-phenyltriazenes[29]. This effect is less clear-cut than the first effect and there are exceptions. For example, the influence of the branching of the alkyl substituent at the keto-group on the ring–chain equilibrium constants for 3-alkyl-1-hydroxyimino-3-propanones[37] is extremely complex and is not correlated with the steric substituent constants E_S.

The 2,6-dimethylphenyl and 9-anthryl residues as well as the analogous condensed systems exert a specific steric influence on the keto-group:



The plane of these substituents has "become detached" from the plane of the keto-group and therefore the *o,o'*-methyl groups of the mesityl substituent, the *peri*-protons of the anthryl substituent, and the oxygen atoms of the condensed dibenzoylenepyridine system prevent the intramolecular nucleophilic attack by the XH group directed at right angles to the plane of the C=O bond. For this reason, the amides of 2-(2,4,6-trimethylbenzoyl)-,[78] 2-(9-anthroyl)-,[79] and 2-[2,3(CO),6,5(CO)-dibenzoyleneisonicotinoyl]-benzoic acids[80] have an open-chain structure regardless of the structure of the substituent at the nitrogen atom and do not cyclise under the conditions of alkaline catalysis. Similar examples are known also for carboxylic acids—2-(2,4,6-trimethylbenzoyl)benzoic and 8-(2,4,6-trimethylbenzoyl)-naphthoic acids[81] and also for the substituted carbinols $2\text{-}R^1COC_6H_4CR_2OH$, where R = Me or Ph and R^1 = 2,4,6-trimethylphenyl[82] or 9-anthryl[83], and for 2-hydroxy-1,4-di-(2,4,6-trimethylphenyl)butane-1,3,4-trione[84].

An increase in the length and branching of the alkyl substituents at the azomethine linkage [R^1 and R^2 in formulae (III)–(VI)] also destabilise the cyclic structure. For example, the ring–chain equilibrium constants for the *N*-(1-hydroxy-1-phenyl-2-propyl)-*N*-methylhydrazones of aliphatic aldehydes[85] decrease with increase of the bulk of the alkyl substituent in the sequence Me < Et < iso-Pr < t-Bu. The same behaviour is observed also for the *N*-2-hydroxy-[50] and 2-mercapto-alkylhydrazones of aldehydes and ketones[53,65] and for the *N*-alkylimines of hydroxycarbonyl compounds[51,55].

IV. THE INFLUENCE OF THE STRUCTURE OF THE CONNECTING UNIT

In order to elucidate the influence of the structure of the connecting unit, systematic studies on the equilibria and rates of the intramolecular reactions between the same two functional groups, while the structure of the carrier system is varied within wide limits, are necessary. Unfortunately, few such investigations, embracing a large set of different structures, have been described in the literature. The ring–chain equilibrium constants have been determined in different investigations under different conditions and by different methods[23], which reduces the value of the information obtained on comparing them.

The problem of the estimation of the influence of the structure of the connecting unit on the ease of formation of the ring and its stability is extremely complex. Two approaches are possible: (1) estimation of the structural possibilities for the mutual approach of the reacting groups in the steric orientation optimum for the intramolecular reaction; (2) assessment of the structure from the standpoint of the entropy and enthalpy contributions (deformation of the bond lengths and angles, non-bonding and electrostatic interactions, strain, etc.) to the energy of formation of the ring[24].

The aim of the expansion of research on these lines was to create a model system whereby one could explain the enormous rates of enzymatic reactions compared with the usual

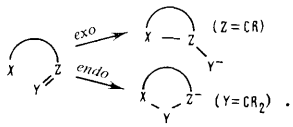
bimolecular reactions. New concepts such as "stereopopulation control"[86-90] and "orbital steering"[91-93] appeared in this connection.

According to the concept of stereopopulation control, the very considerable acceleration of the lactonisation reactions of *o*-hydroxyhydrocinnamic acids, observed after the introduction of methyl groups into the chain and into the benzene ring, can be explained by the increase of the content of the reactive conformer in which both reaction centres have the optimum orientations. It was shown later[94,95] that this effect cannot ensure such a large increase of the rate of reaction and that the increase of the strain energy in the open-chain structure after the introduction of the methyl group plays the most significant role in this phenomenon.

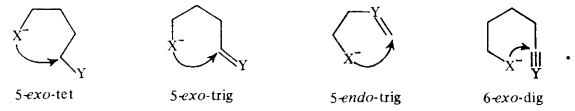
The concept of orbital steering explains the enormous increase of the rate of intramolecular lactonisation of hydroxyacids, achieved by a specific alteration of the structure of the connecting unit, by creating steric conditions for the optimum mutual angular orientation of the reacting centres. This concept has been criticised[96-98] for simplifying the complex pattern of enzymatic reactions and for the clear overestimate of the factor associated with the optimum geometrical orientation of the reacting groups.

Another approach to the solution of this problem[27,99-101] is based on the use of X-ray diffraction data for the crystal structures of specially selected bifunctional compounds in order to elucidate the optimum geometry of the mutual approach of the reacting groups for the minimum-energy reaction. Thus it has been shown on the basis of X-ray diffraction studies on a series of aminoketones that the optimum angle at which the nucleophilic nitrogen atom approaches the C=O bond ($\angle N...C=O$) in nucleophilic addition to the keto-group is ~107° and not 90° as was suggested previously. For the oxygen atom as a nucleophile, this angle is in the range 100–110°.[102]

On the basis of simple considerations concerning the stereochemical requirements of intramolecular reactions, simple empirical laws governing the preferential occurrence of different types of cyclisation have been proposed[103-107]. A convenient classification of such reactions was introduced. The formation of the smaller of the two possible rings is called *exo*-cyclisation and the formation of the larger ring is *endo*-cyclisation:



The prefixes "tet", "trig", and "dig" denote tetrahedral, trigonal, and digonal geometries of the carbon atom attacked by the nucleophile and the numeral denotes the number of members in the ring formed, for example:

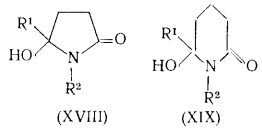


If X is an atom of an element in the Second Period, then 3-, 4-, 5-, 6-, and 7-*exo*-tet-, 3-, 4-, 5-, 6-, and 7-*exo*-trig-, 6- and 7-*endo*-trig-, 5-, 6, and 7-*exo*-dig- and 3-, 4-, 5-, 6-, and 7-*endo*-dig-cyclisation processes are favourable. The 3-, 4-, and 5-*endo*-trig- and 3- and 4-*exo*-dig-cyclisation processes are unfavourable but nevertheless feasible under certain conditions[103].

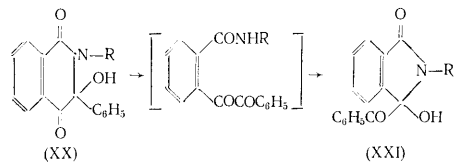
Clearly these rules are most general and the possibility of their practical application is extremely limited, because in the determination of whether or not the cyclisation process is favourable no account is taken of important factors such as the structure of the connecting unit, the presence of the substituents in it, and the nature of the reacting groups. Table 1 presents an example of an unfavourable 5-*endo*-trig-cyclisation, which nevertheless occurs as a ring–chain tautomeric process: aromatic aldehyde *N*-2-hydroxyalkylimine ⇌ oxazolidine#[34].

The rate of formation and higher stability of the five-membered or six-membered cyclic system depend on the nature of the reacting functional groups and the structure of the unit connecting them.

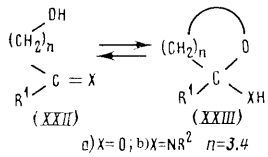
With an appropriate choice of substituents R^1 and R^2, the amides of 3-acylpropionic acids form stable five-membered hydroxylactams (XVIII),[39,108] while it is altogether impossible to obtain the six-membered hydroxylactams (XIX) from similarly substituted amides of 4-acylbutyric acids:



The higher stability of five-membered hydroxylactams compared with the six-membered compounds is confirmed by their ready isomerisation with ring contraction: (XX) → (XXI):[109,110]



On the other hand, in the series of 3-acylpropanols and 4-acylbutanols [(XXIIa) ⇌ (XXIIIa)], the ring–chain equilibrium constants are higher[111] for the closure of the six-membered ring. This also applies to their *N*-alkylimines [(XXIIb) ⇌ (XXIIIb)]:[51]

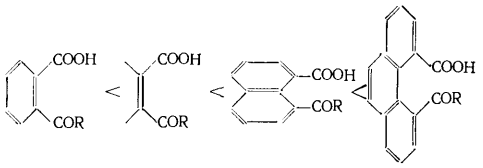


It is seen from a comparison of the rate constants for a large set of cyclisation reactions (see Table 13 in the monograph of Capon and McManus[7]) that a five-membered ring is formed more readily than a six-membered ring in the intramolecular substitution at a tetrahedral carbon atom when the connecting unit consists of sp^3-carbon atoms. The relative ease of closure of the six-membered ring increases after the introduction of sp^2-carbon atoms in the chain and also for reactions involving intramolecular addition to a trigonal carbon atom.

A series of acyl-substituted carboxylic acids, in which the stability of the cyclic form increases for identical substituents R in each respective instance have been proposed[33];

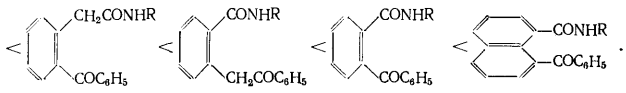
#An example of the faster "unfavourable" 5-*endo*-trig-cyclisation compared with the "favourable" 6-*endo*-trig-cyclisation process has also been observed by J.B.Lambert and M.V.Majchrzak (J.Amer.Chem.Soc., 1980, **102**, 3588).

the ring–chain equilibrium constants have been published in a monograph[23] (Table 3):



An increase in the stability of the cyclic form in an analogous series has been observed[23,38] for the amides of 3- and 4-benzoyl-substituted carboxylic acids:

$C_6H_5CO(CH_2)_3CONHR < C_6H_5CO(CH_2)_2CONHR <$



The influence of the structure of the connecting unit on the equilibrium and rate constants for the lactonisation and thiolactonisation reactions of hydroxy- and mercapto-acids has been examined (Table 2)[92,93]; these data have been compared with the rate constants for the corresponding intermolecular reactions. It can be easily shown that insignificant changes in the structure of the connecting unit can have an enormous influence on the rate and equilibrium of the intramolecular reaction. Comparison of lactonisation and thiolactonisation (Table 2) shows clearly that the same structure of the carrier system has different effects on the rates of these reactions: the ratio of the lactonisation and thiolactonisation rate constants varies within the limits of two orders of magnitude, although the overall trend is maintained.

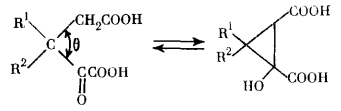
It is seen from the examples presented that the ease of formation and the stability of the cyclic form (the heterocycle) increase with increase of the rigidity of the connecting unit, i.e. with decrease of its conformational mobility, provided that the possibility of the mutual approach of the reacting groups in space and their optimum mutual orientation are maintained. Thus, in the structures of carboxylic ketoacids and their amides which have been examined, the keto-group is capable of free rotation about the C–CO bond and of assuming a conformation in which the nucleophile (O or N) can approach its plane in a perpendicular direction. The failure of this condition in the molecules of anthraquinone-1-carboxylic acid[116] prevents cyclisation.

The elucidation of the general characteristics of the influence of the structure of the connecting unit on the rate and equilibrium constants for the intramolecular reactions is difficult owing to the difference between the steric requirements of different reacting groups. The examples considered and the data in Table 2 show that there are no direct correlations between the structure of the connecting unit and the $\lg K$ and $\lg k$ for intramolecular reactions when pairs of reacting groups are replaced.

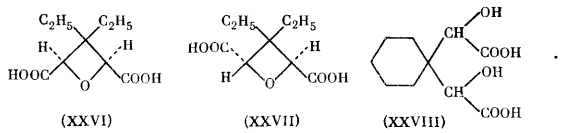
V. STERIC EFFECTS OF SUBSTITUENTS IN THE CONNECTING UNIT

1. The Thorpe–Ingold Effect

The introduction of alkyl groups at carbon atoms in the chain between the reacting groups and particularly the introduction of two groups at the same atom increase the rate of cyclisation and shift the equilibrium in the direction of the cyclic structure. This effect is usually called the "*gem*-dimethyl", "*gem*-dialkyl", or "Thorpe–Ingold" effect[1,2,7–9,16]. The first theoretical explanation has been given by Thorpe and Ingold[117,118], who observed the effect in a ring–chain isometric system which they suggested involved the (XXIV) ⇌ (XXV) transformation. A sharp increase of the content of the cyclic isomer was observed after the introduction of two alkyl groups R^1 and R^2 and the increase of their bulk[119]. The authors explained this phenomenon by the decrease of the valence angle θ.



(XXIV) (XXV)



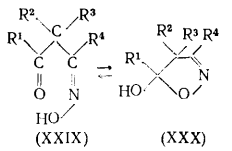
(XXVI) (XXVII) (XXVIII)

However, structures (XXIV) and (XXV) were later disproved by ^1H NMR and the corrected structures (XXVI)–(XXVIII) were proposed in their place[120,121]; this greatly reduced the popularity of Ingold's concept. The study of the intramolecular hydrogen bond in 2-substituted propane-1,3-diols by infrared spectroscopy showed[18] that, after the introduction of substituents at the middle carbon atom, the C–C–C angle decreases somewhat, but this decrease cannot play a significant role in the closure of five- and six-membered rings.

Hammond[1] saw a more important cause of the influence of the *gem*-dialkyl group on the cyclisation reaction in the restriction of the free rotation about the C–C–C bonds in the open-chain isomer after the introduction of two bulky groups at the middle carbon atom and hence in the appearance of entropy factors favouring cyclisation. As a development of this idea, a thermodynamic concept based on a comparison of the enthalpies and entropies of linear and cyclic structures was proposed[122]. It has been shown for hexanes and cyclohexanes that, in the presence of alkyl substituents, there is a smaller number of non-bonding *gauche*-interactions in the rings than in open chains. This implies that the enthalpy factors favour cyclisation of the methyl-substituted chain to a greater extent than the unsubstituted chain. Furthermore, branching reduces the entropy of open-chain compounds by restricting the internal rotation, but cannot alter significantly the entropies of cyclic compounds, because they are capable of free internal rotation. The decrease of ΔH and the increase of ΔS for the cyclisation reactions of pentane and hexane in the gas phase after the introduction of two methyl groups at the same carbon atom lead to an increase of the equilibrium constant by 2–3 orders of magnitude[7] (p.59).

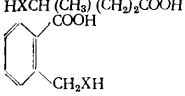
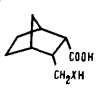
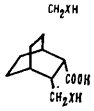
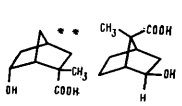
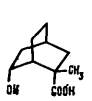
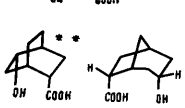
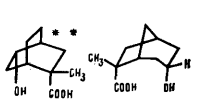
In a study of the ring–chain tautomerism of 1-hydroxyimino-3-propanones [(XXIX) ⇌ (XXX)], it was observed[37] that in solutions of 3-methyl-4-spiropropano-5-hydroxy-5-phenyl-Δ^2-isoxazoline [XXX, R^1 = Ph, R^2, $R^3 = -(CH_2)_2$, R^4 = Me] and the corresponding 4,4-dimethyl derivative (XXX, R^1 = Ph, $R^2 = R^3 = R^4$ = Me) the open-chain tautomeric form is absent within the limits of the sensitivity of the infrared spectroscopic and ^1H NMR methods. Since the equilibrium (XXIX) ⇌ (XXX) has been observed for the 4-unsubstituted derivative, this finding disproves Ingold's concept, since $(CH_2)_2C\langle$ angle has not been reduced and has even been increased conpared with the $H_2C\langle$ angle. The stabilisation

of the cyclic isomer (XXX) on spirocyclopropane substitution in the 4-position can be accounted for only by the restriction of the freedom of rotation or by the appearance of steric strain in the open-chain isomer of isoxazoline (XXIX):



(XXIX) (XXX)

Table 2. The influence of the structure of the connecting unit on the equilibrium and rate constants for the lactonisation of carboxylic hydroxy- and mercapto-acids under the conditions of acid catalysis[92,93].

Carboxylic hydroxy- or mercapto-acid	X = O		X = S	
	K	$\lg k_{rel}$	K	$\lg k_{rel}$
$CH_2CH_2XH + CH_3COOH$ *	$7\cdot10^{-2}$	0.00	$6.6\cdot10^{-4}$	0.00
$HX(CH_2)_2COOH$	6.15	1.90	2.44	2.58
$HXCH(CH_3)(CH_2)_2COOH$	11.13	2.07	—	—
	—	2.50	—	2.97
	2810	3.82	110	1.95
	—	5.14	63	3.67
	12740	6.01	>100	5.91
	—	2.44	—	—
	—	2.94		
	—	4.99		
	—	3.96		
	—	5.68		

*The rate constants adopted as unity actually amount to $k = 1.09 \times 10^{-3}$ litre mol^{-1} min^{-1} for X = O and $k = 3.2 \times 10^{-6}$ litre mol^{-1} min^{-1} for X = S.

**These structures shown in brackets proved to be erroneous in a reinvestigation[112–115]; the corrected structures are shown next to them.

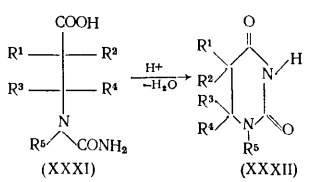
The positive influence of alkyl substituents in the connecting unit on the rate and equilibrium constants has been observed in the conversion of succinic acids[123] and their *N*-phenyl monoamides[124] into anhydrides [and imides respectively?], the lactonisation of 4-hydroxybutyric and 5-hydroxyvaleric acids[125], in the ring–chain tautomerism of levulinic acids[126], many other ring–chain tautomeric systems[20, 23,50], addition reactions with intramolecular cyclisation[127], intramolecular catalysis proceeding via a cyclic transition state[5–9], and the formation of an intramolecular hydrogen bond[17].

The influence of alkyl substituents on the rate and equilibrium constants for cyclisation reactions depends on their bulk, their position in the connecting unit, and the conformational mobility of the connecting unit itself. If the reacting groups are separated by a chain of three sp^3-carbon atoms, the introduction of alkyl substituents at the middle atom has the greatest influence[125,128]. The methyl groups at the carbon atom in the α-position relative to the reacting group, particularly the C=O group, can have the opposite influence owing to the steric shielding of the reaction centre. The influence of the position of the methyl substituent can be followed in relation to the cyclisation of methyl-substituted 3-ureidopropionic acids [(XXXI) → (XXXII)] (Table 3)[129].

Table 3. The influence of methyl substituents on the rate constants for the cyclisation of 3-ureidopropionic acids [(XXXI) → (XXXII)].[129]

R^1	R^2	R^3	R^4	R^5	$\lg k_{rel}$
H	H	H	H	H	0.00
Me	H	H	H	H	0.07
H	H	Me	H	H	0.45
erythro-Me	H	Me	H	H	−0.08
threo-Me	H	H	Me	H	0.47
Me	Me	H	H	H	−0.46
H	H	Me	Me	H	1.25
H	H	H	H	Me	1.66

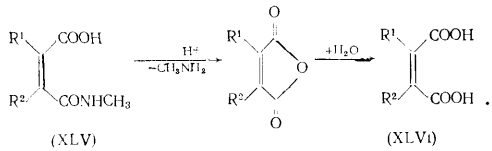
The introduction of two methyl groups in the α-position relative to the carboxy-group actually retards cyclisation, while two methyl groups at the β-carbon atom greatly accelerate it.



(XXXI) (XXXII)

The destabilisation of the cyclic structure after the introduction of the methyl group at the carbon atom in the α-position relative to the C=O group has been observed in the ring–chain tautomerism of *N*-(3-oxoalkyl)-*N'*-substituted thioureas[70] and 3-aryl-1-(2-oxoalkyl)triazenes[29].

The influence of alkyl substituents at an sp^3-carbon atom intensifies following the increase of the conformation rigidity of the connecting unit, which is readily seen in relation to the lactonisation reactions (XXXIII) → (XXXIV) and (XXXV) → (XXXVI) (Table 4)[130].

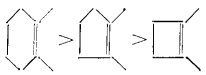


(XLV) (XLVI)

Table 6. The influence of alkyl substituents at the sp^2-carbon atoms on the ring–chain equilibrium constants K for *cis*-3-acetylacrylic acids [(XLIII) → (XLIV)] [143] and the hydrolysis rate constants k_{rel} for *N*-methylmaleamic acids [(XLV) → (XLVI)]. [142]

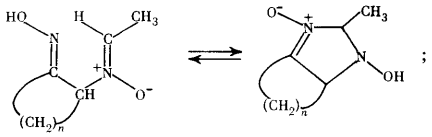
R^1	R^2	$\lg K$ (XLIII) ⇄ (XLIV)	$\lg k_{rel}$ (XLV) → (XLVI)
H	H	1.2	0.00
Me	H	1.9	1.49
H	Me	3.6	—
Me	Me	5.2	4.37
	$(CH_2)_4$	—	2.73
	$(CH_2)_3$	—	−4.38
	$(CH_2)_2$	—	−5.38

On passing to cyclopentene and cyclobutene systems, the catalytic effect of the carboxy-group disappears, which can be explained by the alteration of the valence angles in the sequence



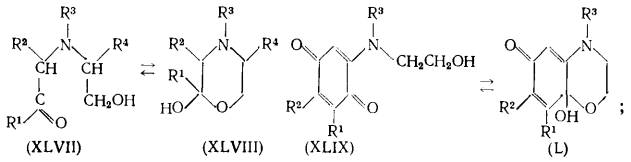
which is unfavourable for the formation of a cyclic transition state.

An analogous influence of ring size has been observed [144] in the ring–chain tautomerism of *N*-(2-hydroxyiminocycloalkyl) nitrones:

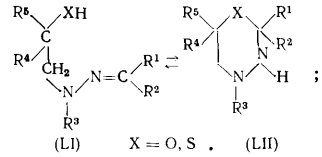


$n = 5$, $K > 100$; $n = 4$, $K = 9$; $n = 3$, $K = 0$.

The introduction of an alkyl group at the nitrogen atom in the connecting unit leads to a marked stabilisation of the cyclic structure (Table 3), which has been demonstrated in relation to the ring–chain tautomerism of *N*-alkyl-*N*-(2-hydroxyalkyl)-*N*-(2-oxoalkyl)amines [(XLVII) ⇌ (XLVIII)], [145, 146] 2-*N*-alkyl-*N*-(2-hydroxyethyl)amino-1,4-benzoquinones [(XLIX) ⇌ (L)], [147] and *N*-alkyl-*N*-(2-hydroxy- or 2-mercapto-alkyl)hydrazones of aldehydes and ketones [(LI) ⇌ (LII)]: [50,52,53,65,148,149]



(XLVII) (XLVIII) (XLIX) (L)



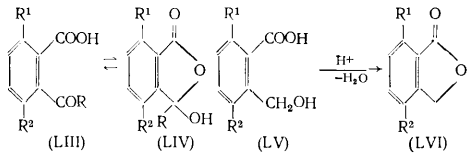
(LI) X = O, S . (LII)

The introduction of alkyl substituents R^3 and the increase of their bulk displace the equilibrium towards the cyclic form, while in the absence of a substituent at the nitrogen atom (i.e. for $R^3 = H$), compounds (XLVII), (XLIX), and (LI) exist preferentially in the stable open-chain form and a tautomeric equilibrium is not observed.

Potekhin and Bogan'kova [149] suggest the weakening of the intramolecular hydrogen bond X–H...NR^3 as one of the possible causes of the destabilisation of the open-chain structure (LI) with increase of the bulk of the substituent R^3 in addition to the entropy factor, but they do not present any experimental evidence for this hypothesis.

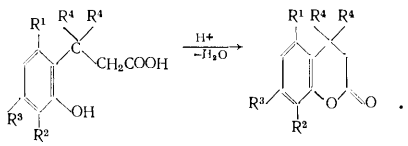
2. The "Supporting" or Steric Cooperation Effect

If the reacting groups are in the *ortho*-positions in an aromatic ring, then the neighbouring alkyl or other substituents give rise to a steric strain, which favours intramolecular cyclisation [150]. Such influence is called the "supporting" or steric cooperation effect. Table 7 presents the quantitative characteristics of this effect for the ring–chain tautomerism of 2-acetylbenzoic [151] and 2-benzoylbenzoic [152] acids [(LIII) ⇌ (LVI)] and also for the lactonisation of 2-hydroxymethylbenzoic acid [(LV) → (LIV)], [153]



(LIII) (LIV) (LV) (LVI)

and 3-(2-hydroxyphenyl)propionic acid [(LVII) → (LVIII)]: [86,87]



(LVII) (LVIII)

The gradual introduction of methyl groups into the molecule of 3-(2-hydroxyphenyl)propionic acid (LVII) makes it possible to discover the influence of the location of the methyl substituents on the lactonisation rate constants under the conditions of acid catalysis; the maximum acceleration attained under these conditions is by 11 orders of magnitude. The main driving force of the acceleration of lactonisation after the introduction of methyl substituents is steric strain in the ground state of the initial molecule and from this standpoint there is no fundamental difference between the Thorpe–Ingold effect [as in compound (LVII, R^4 = Me)] and the steric cooperation effect [as in compound (LVII, $R^1 = R^2$ = Me)].

It is seen from Table 7 that the accelerating effect depends on the bulk of the substituent in the *ortho*-position with respect to the position where the methyl group is to be introduced. The introduction of the methyl group in the

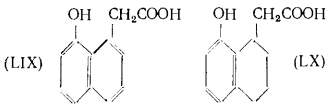
ortho-position with respect to the OH group or the introduction of two methyl groups in the *ortho*-positions with respect to the OH and CH_2CH_2COOH groups accelerates lactonisation by a factor of 3–7, while the methyl group in the *ortho*-position with respect to the CMe_2CH_2COOH group accelerates the lactonisation reaction by 7 orders of magnitude. The extremely high acceleration of the lactonisation reaction (LVII) → (LVIII) has been explained by the fact that the methyl substituents R^1, R^2, and R^4 restrict the freedom of rotation about the C–C bonds and favour the preferential formation of the conformation in which both reacting groups are in the optimum position for reaction between them[86,87].

Table 7. The steric cooperation of the *ortho*-substituents in cyclisation reactions.

R^1	R^2	K ((LIII) ⇄ (LIV))		$\lg k_{rel}$ ((LV)→(LVI)) [153]	$\lg k_{rel}$ ((LVII)→(LVIII)) [86,87]	
		R=Me [151]	R=Ph [152]		R^4=H	R^4=Me
H	H	3.2	<0.1	0.00	0.00*	3.65*
Me	H	16	2.85	1.19	—	10.93**
H	Me	0.52	0.22	1.72	—	4.22*
Me	Me		13.3	2.50	0.83**	11.41*
						11.53**

*R^3 = H.
**R^3 = Me.

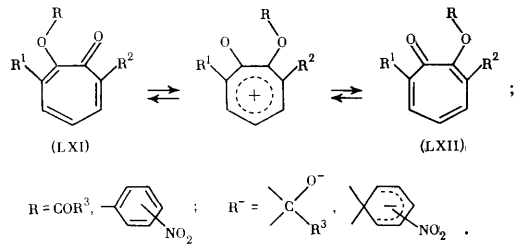
It has been shown[94] that such high acceleration of cyclisation on passing from compound (LVII, $R^1 = R^2 = R^3 = R^4 = H$), i.e. compound (LVIIa), to the trimethyl-substituted compound (LVII, $R^1 = R^2 = R^4 = Me$, $R^3 = H$), i.e. compound (LVIIb), which is by a factor of 10^{11}, cannot be caused solely by the presence of the optimum conformation (this has been confirmed by X-ray diffraction analysis[90]); the steric strain in the initial molecule plays a more significant role here. Comparison of the rate constant for the lactonisation of the acid (LVIIa) with the lactonisation constants for 8-hydroxynaphthylacetic acid (LIX) and 8-hydroxy-1,2,3,4-tetrahydronaphthylacetic acid (LX),



(LIX) (LX)

which model the fixed most favourable conformation for the lactonisation reaction ($k_{(LIX)}/k_{(LVIIa)} = 2.1 \times 10^4$; $k_{(LX)}/k_{(LVIIa)} = 1.5 \times 10^2$) shows that acceleration by a factor of only 10^4 is ensured by the most favourable conformation. The remaining contribution to the acceleration of the cyclisation reaction on passing from compound (LVIIa) to (LVIIb), amounting to a factor of ~10^7, is due to the enthalpy effect of the steric strain in the initial molecule, which has been confirmed by empirical force field calculations[95].

The steric cooperation effect is clearly manifested in the acylo- and arylo- tropic tautomerism of the tropolone system [(LXI) ⇌ (LXII)]:[12,154–156]



The introduction of methyl or benzyl substituents in the 3- and 7-positions in the tropolone ring has a favourable steric effect on the formation of a cyclic dipolar transition state or intermediate and accelerates the migration of acyl or aryl groups. In the presence of only one methyl substituent (R^1 = Me, R^2 = H, R = Me_2NCO), the equilibrium (LXI) ⇌ (LXII) is displaced towards the sterically less encumbered tautomer (LXII) (K = 4).[156]

It is seen from the examples considered (see also Capon and McManus[7]) that the influence of the alkyl substituents in the connecting unit on the cyclisation reactions depends on many factors and is difficult to predict quantitatively. Progress in this field resulting from the employment of computational methods has been noted recently.

A satisfactory linear correlation (r = 0.932–0.993) between the free energies of activation for the cyclisation reactions of methyl-substituted ureidopropionic acids [(XXXI) → (XXXII)] and also a number of previously investigated anhydride formation reactions of succinanilic[124] and succinic[123] acids, the hydrolysis of p-bromophenylglutarates [(XLI) → (XLII)],[131] and the lactonisation of 4-hydroxybutyric and 5-hydroxyvaleric acids[125], on the one hand, and the energies of the steric strain estimated on the basis of the enthalpies of formation of homomorphous hydrocarbons[157], on the other, has been observed recently[129].

Empirical force field calculations[150,158–163] have been used successfully for the quantitative prediction of the acceleration of the lactonisation of carboxylic hydroxyacids when the structure of the connecting unit is altered and methyl substituents are introduced[95,164].

The possibilities of the computational methods have been satisfactorily demonstrated[165,166] for the cyclisation reactions of bromoalkylamines and their derivatives substituted by alkyl groups in the chain. A satisfactory agreement between the calculated and experimental rates of cyclisation was observed; the enthalpies of activation were calculated by the empirical force field method and the entropies of activation were obtained from the analogous formal cyclisation reactions of homomorphous alkanes.

It has been confirmed by computational methods that the driving force of the Thorpe–Ingold effect is mainly the enthalpy factor and not the entropy factor as was believed previously[86,87].

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Spectroscopy of Intermolecular Field Interactions in Solutions

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Methods of interpreting data on the effect of the solvent on the spectral characteristics of molecules are critically compared. It is shown that the effect of field-induced intermolecular interaction in solutions on molecular spectra can be calculated in terms of the London-Debye-Keesom pair potential. 145 references.

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I. INTRODUCTION

Condensed media, in which the distance between molecules is smaller than in gases, invariably show substantial interaction between molecules with saturated chemical bonds (intermolecular interaction, IMI). The features of the IMI determine the thermodynamic properties of liquids and the kinetics and mechanisms of the elementary chemical acts: the IMI also control the formation of donor–acceptor complexes, and are responsible for the formation of colloidal systems. In biological systems intermolecular forces control the stability of all the compounds which are essential to life.

Intermolecular interactions can be studied experimentally by a variety of methods[1], mostly spectroscopic[2]. The interactions reveal themselves in the spectra of molecules in different ways (shifts in the absorption and in the emission bands, changes in intensity and shape of the bands, appearance of new bands). Information on the nature of the IMI can be obtained also from measurements of the polarisation and dipole moments of molecules[3,4].

All the different types of IMI can be classified into two main groups. Terenin[5] subdivides intermolecular forces into physical (determined by the physical characteristics of the interacting molecules) and chemical (responsible for the formation of directional chemical or quasi-chemical bonds between molecules). Other workers[6,7] classify the IMI into volume interactions (in which each molecule is bound to surrounding molecules by a force inversely related to distance) and local interactions (in which two or more molecules are held together fairly strongly but the bonds between these groups of molecules have only secondary importance). Others[8-10] distinguish between short-range and long-range order when classifying intermolecular forces. The former involves interactions described in terms of the physical parameters of the molecules, whereas the latter involves valency or chemical forces arising from overlap of the electron clouds of the interacting molecules. Bakhshiev[2] suggests classifying the IMI not according to their forces or radii of action, but according to the "generality of their occurrence". He classifies all types of IMI as universal or specific. The former operate between molecules in all systems, without exceptions, and are determined by the physical parameters of the molecules: they describe the collective influence of the surrounding molecules on the properties of one particular molecule. The specific IMI do not occur in all systems: they are individual manifestations, confined to a particular pair of interacting molecules. They have a quasi-chemical (exchange) origin and a high degree of selectivity towards certain molecules, leading to the formation of a definite bond which can be strong or weak[2].

In spite of these differences in terminology, and in the light of the physical meaning of the term IMI, we shall use the following classification of the IMI into two groups: the first group includes the van der Waals interactions, which are additive and non-directional (attractive forces due to orientation, induction, and dispersion effects, and repulsive forces arising from the mutual impenetrability of molecules), and the second group includes all forms of interaction of donor–acceptor origin and showing the typical attributes of a chemical bond (saturability and directionality).

The interaction energy of two molecules can be expressed as the sum $U_{tot} = U_{or} + U_{ind} + U_{dis}$, where the terms in the right-hand side denote the energies arising from the orientation, induction, and dispersion interaction of the molecules, given by the London–Debye–Keesom formulae[11] as

$$U_{or} = -\frac{2\mu_1^2\mu_2^2}{3kT\bar{R}^6},$$

$$U_{ind.} = -(\alpha_1\mu_2^2 + \alpha_2\mu_1^2)/\bar{R}^6, \quad U_{dis} = -\frac{3}{2}\frac{I_1I_2}{(I_1+I_2)}\frac{\alpha_1\alpha_2}{\bar{R}^6}.$$

In these expressions $\bar{R}$ is the average distance between the molecules, μ_1 and μ_2 are the (constant) dipole moments, α_1 and α_2 are the isotropic polarisabilities, and I_1 and I_2 are the first ionisation potentials of the molecules.

A strict solution of the intermolecular interaction problem (and an exact calculation of U_{tot}) are possible by using quantum mechanics. This calculation (so far attempted only for the simplest molecules) yields the interaction energy of the molecules as a function of the intermolecular distance $\bar{R}$. For more complex molecules the quantum-mechanical calculation becomes unacceptably laborious, and empirical models of the intermolecular potential are used to calculate the IMI energy. Depending on the properties of the system, the Lennard-Jones, Morse, Kihara, Stockmaier, Buckingham, and other potentials have all been widely used. For example, the well-known Lennard-Jones potential

$$U(r) = E\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

(where E is the minimum potential energy of the pair of molecules, σ is the distance for which U is a minimum, and r is the Onsager radius of the molecule) ignores many-particle interactions and does not explicitly allow for the parameters I, α, and μ, which (together with the structural parameters $\bar{R}$ and $\bar{Z}$, the number of nearest neighbours) determine the value of U.

In this review we shall attempt to generalise the large amount of published data on the determination of the IMI energy by using the theoretically well-justified London–Debye–Keesom potential for the pair interactions between

molecules in a liquid in order to study the spectral characteristics of molecules in solutions.

II. EFFECT OF THE MEDIUM ON THE I.R. SPECTRA OF MOLECULES AND COMPLEXES

1. Methods of Calculating the Effect of the Medium on the I.R. Spectra

Two types of relationship between the spectral characteristics and the properties of the solvent are generally used to allow for the IMI effects of a universal type on the characteristics of the vibrational spectra of molecules in solutions: those involving macroscopic parameters such as the dielectric constant ε and the refractive index n, and those involving molecular parameters such as the dipole moment μ, the polarisability α, and the ionisation potential I. The first group includes relationships based on potentials for the collective interation between solvent and solute molecules. Kirkwood[12], and Bauer and Magat[13], used the Onsager reactive field model[14] to derive the widely used expression (KBM formula)

$$\frac{\Delta\nu}{\nu_s} = \frac{\nu_s - \nu_{gas}}{\nu_{gas}} = -C\,\frac{\varepsilon - 1}{2\varepsilon + 1}\ .$$

Buckingham[15] replaced ε by n^2 in this formula, converting the KBM formula into

$$\frac{\Delta\nu}{\nu_s} = \frac{\nu_s - \nu_{gas}}{\nu_{gas}} = -C\,\frac{n^2 - 1}{2n^2 + 1}$$

where ν_{gas} is the stretching vibration frequency of the isolated molecule, ν_S is the vibration frequency in the medium, $\Delta\nu$ is the frequency shift, C is a constant depending on the properties of the solute molecule, and ε and n are the dielectric constant and the refractive index of the solvent respectively.

However, these expressions have had only limited success with both polar[16,17] and non-polar solvents[18], and they cannot be applied to systems in which $\nu_S > \nu_{gas}$ to calculate the vibration frequency of groups able to form H-bonded complexes[2].

The KBM theory was further developed by Pullin[19], who examined the effect of the solvent on the spectrum of the solute in terms of ε, n, the molar volume of the solvent, and the molar volume of the solute. However, in Pullin's expression

$$\frac{\Delta\nu}{\nu_0} = C + \frac{A}{R}\,\frac{n^2 - 1}{n^2 + 2} + B\,\frac{\varepsilon - 1}{2\varepsilon + 1}$$

(where A and B are constants, and R is the radius of a sphere circumscribing the molecule) the physical significance of the constants is not clear, and the ratio A/R is found to depend on the nature of the medium.

The work of Buckingham, based on quantum-mechanical considerations, is especially interesting[20]. By using first- and second-order perturbation theory he obtained an expression for the relative frequency shift of the absorption corresponding to the transition between levels with vibrational quantum numbers m and n,

$$\frac{\Delta W_{m,n}}{W_{m,n}} = \frac{B_e}{hcW_e^2}\left[\bar{U}'' - 3\,\frac{A}{W_e}\,\bar{U}'\right]\ ,$$

where B_e is the rotational constant, A/W_e is the anharmonicity constant of the vibration, and U' and U'' are the first and the second differential of U (the interaction energy of the solute molecule with the solvent molecules) with respect to the vibration coordinate.

By applying the Onsager reactive field theory Buckingham[20] arrived at the following expressions for the relative frequency shifts in non-polar solvents,

$$\frac{\Delta\nu}{\nu} = C_1 + \frac{1}{2}\,C_2\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) + \frac{1}{2}\,C_3\,\frac{n^2 - 1}{2n^2 + 2}\ ,$$

and in polar solvents,

$$\frac{\Delta\nu}{\nu} = C_1 + C_2\,\frac{\varepsilon - 1}{2\varepsilon + 1} + C_3\,\frac{n^2 - 1}{2n^2 + 2}\ ,$$

where C_i are constants determined by the microscopic characteristics of the molecules in solution (polarisability, dipole moment, etc.).

The most important attribute of these expressions is the fact that the physical meaning of their constants is relatively clear, though their application is limited to diatomic molecules. Attempts to apply them to polyatomic molecules[21] by calculating all the C_i values from experimental $\Delta\nu$ values are physically meaningless. This is especially true of the expressions which include a fourth term ($C_4\sigma^*$) to allow for the specific interactions of the molecules in solution[18,22].

From the Onsager model Bakhshiev obtained[2] the following expression for the shift in vibration frequency:

$$H\Delta\nu = -\Delta R\left[\frac{\mu_0\left(\frac{\partial\mu_0}{\partial R}\right)_{R_{s,d}}(F_1 + F_2)}{1 - \alpha_0(F_1 + F_2)}\left(\frac{\partial\alpha}{\partial R}\right)_{R\,equil} F_3\right];$$

$$F_1 = \frac{2}{a^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\varepsilon_\infty - 1}{2\varepsilon_\infty + 1}\right);\quad F_2 = \frac{1}{a^3}\left(\frac{\varepsilon_\infty - 1}{2\varepsilon_\infty + 1}\right);$$

$$F_3 = \frac{3}{2a^3}\,\frac{I_s I_d}{I_s + I_d}\left(\frac{n^2 - 1}{n^2 + 2}\right)\ ,$$

where H_ν is the energy, and the subscripts 0, s, and d denote the gas phase, the solvent, and the dissolved substance (throughout this paper). This expression includes, in addition to macroscopic properties of the medium, also parameters which characterise the properties of the solute molecules. However, the relationship is difficult to apply, even to diatomic molecules[2,23,24]. In the case of more complex molecules the difficulties in determining the molecular parameters and in defining rationally the Onsager radius of the mole (a) become almost insuperable. Furthermore, the presence of macroscopic parameters of the solvent in the expression destroys the clarity of the presentation of the dependence of $\Delta\nu$ on the molecular properties of the solvent and makes it impossible to correlate $\Delta\nu$ with the basic characteristics of the molecular structure of the liquid.

The limited possibilities of all expressions which include generalised parameters of the solvent led to the belief that the universal IMI are always accompanied by specific interactions, or even that their effect is negligible and limited to the formation of low-stability complexes. The former point of view is implicit in the Caldow and Thompson expression[22]

$$\Delta\nu = C_1 + C_2\,\frac{\varepsilon - 1}{2\varepsilon + 1} + C_3\,\frac{n^2 - 1}{n^2 + 2} + C_4\sigma^*\ ,$$

where σ^* allows for the inductive or resonance effect of the substituents in the solvent molecule. The latter point of view is expressed in the work of Bellamy[25-27], who studied the correlation of the $\Delta\nu/\nu$ values for different vibrators in the same series of solvents. These workers assumed[22,25-27] that specific interactions can occur in non-polar as well as in polar solvents.

These views were further developed[28,29] in the cell theory of liquids. Using the terminology of that theory, strong specific interaction can be related mainly to the formation of donor–acceptor complexes in systems of the "polar solute–polar solvent" type, and weak non-specific interaction to the formation of collision complexes in systems of the "polar solute–non-polar (or weakly polar) solvent" type. This treatment excludes from the start any possibility of revealing characteristic dependences of the solvent effect on the composition and structure of the molecules for different types of IMI.

Another group of expressions for calculating the effect of IMI on $\Delta\nu$ relies on the pair interaction potential concept. The first expression of this type was proposed by Vol'kenshtein[30], who calculated the potential energy of the van der Waals interaction between solvent–solute pairs of molecules in the approximation of the London–Debye–Keesom potential:

$$U = \frac{1}{\bar{R}^6}\left(\frac{2}{3kT}\mu_s^2\mu_u^2 + \mu_s^2\alpha_d + \mu_d^2\alpha_s + \frac{3}{4}I\alpha_s\alpha_d\right).$$

Solution of the equations of motion leads to the following expression for the normal vibration frequency of the system:

$$\Delta W = WW_0 = -\frac{1}{2}\frac{B}{mW_0} \pm \frac{A}{mW_0},$$

where m is the reduced mass, and A and B are the sums of coefficients describing the orientation (o), dispersion (α), and induction contribution (i) to the pair interaction:

$$A = A_o + A_i + A_\alpha;\ B = B_o + B_i + B_\alpha .$$

The frequency shift is given by the factor B/mW_0, the line broadening by A/mW_0, with

$$B_0 = \frac{4}{3kT\bar{R}^6}\left[\mu^2\left(\frac{\partial\mu}{\partial q}\right)^2 + \mu^3\frac{\partial^2\mu}{\partial q^2}\right];\ B_\alpha = \frac{3}{4}\frac{I}{\bar{R}^6}\alpha\frac{\partial^2\alpha}{\partial q^2};$$

$$B_i = \frac{2}{\bar{R}^6}\left[\alpha\left(\frac{\partial\mu}{\partial q}\right)^2 + \alpha\mu\frac{\partial^2\mu}{\partial q^2} + \mu^2\frac{\partial^2\alpha}{\partial q^2}\right].$$

In these expressions $\bar{R}$ is the distance between dipoles, q is the relative displacement from the equilibrium position, μ is the dipole moment of the molecule, $\partial\mu/\partial q$ is the effective charge on the dipole, and $\partial^2_\mu/\partial q^2$ is the electrical non-linearity of the dipole.

Vol'kenshtein and coworkers[31] included not only the dipole–dipole inductive and dispersion interaction energy in their calculation of the IMI in terms of pair interaction energies, but also the repulsive energy of the molecules. The energy of the interaction between two molecules was identified with the sum of the pair interactions between bonds[32]. In this way, ignoring the second differential with respect to the vibration coordinate, we can arrive at the following expression for $\Delta\nu$ in the case of solutions of a polar substance in a non-polar solvent:

$$\Delta\nu = -\frac{3K_{11}}{8\pi^2c^2M_2V}\left[\frac{\alpha'_d}{\alpha_d} - 6\frac{R'_{s,d}}{R_{s,d}} + \frac{I'_d}{I_d} - \frac{I'_d}{I_d+I_s}\right]E_{disp} \qquad (1)$$

and for a polar solute in a polar solvent

$$\Delta\nu = -\frac{3K_{11}}{8\pi^2c^2M_2V}\left\{\left[\frac{\alpha'_d}{\alpha_d} - 6\frac{R'_{s,d}}{R_{s,d}} + \frac{I'_d}{I_d} - \frac{I'_d}{I_d+I_s}\right]E_{disp} + \right.$$

$$\left. + \frac{2\mu'_d}{\mu_d}E_{disp} + \left[\frac{\mu'_d}{\mu_d} - 3\frac{R'_{s,d}}{R_{s,d}} + \frac{I'}{I}\right]E_{or} - \left[\frac{a'}{a} - b'R_{s,d}\right]E_{rep}\right\}, \qquad (2)$$

where α', I', and μ' are the differentials with respect to the vibration coordinate of the polarisability, the ionisation potential, and the dipole moment respectively, $R_{s,d}$ is an orientation factor, a' and b' are the constants in the exponential expression for the repulsive energy, c is the velocity of light, M is the reduced mass of the molecule, ν is the frequency, and K is the force constant.

Acceptably precise calculations of $\Delta\nu = \nu_s - \nu_{gas}$ for quite simple molecules present almost insuperable difficulties in the evaluation of the pair interaction potential (as in the case of the potentials based on the collective interaction of molecules in solution). This explains the growing practice of correlating $\Delta\nu$ with various empirical parameters of the solvent[16,33]. However, the main advantage of using the pair interaction potential is the explicit presence in this type of expression for E_{in} of the molecular properties of the solvent (μ_s, α_s, I_s) as well as those of the solute, and also the explicit presence of characteristics of the molecular structure of the solution (Z and $R_{s,d}$). Unlike the expressions relying on collective interactions, the pair interaction relationships make it possible to study the dependence of $\Delta\nu$ on various specific properties of both the solvent and the solute molecule, and also its dependence on $\bar{Z}$ and $\bar{R}_{s,d}$. Thus, by using Eqns.(1) and (2) we can calculate E_{or} from the Keesom expression for the orientation interaction averaged over all configurations ($E_{or} \cong \mu_s^2\mu_d^2/\bar{R}^6$) instead of the expression for the local interaction, which makes it unnecessary to calculate I. Since α'_d is negligibly small, and α_d is almost independent of the nature of the solvent, but μ'_d varies with μ_d, we can expect that for a given solute in a series of solvents with similar values of I_s and $\bar{R}_s$ (and therefore similar values of $\bar{R}_{s,d}$) the combined contribution to $|\Delta\nu|$ from all the effects associated with the change of solvent will be quite small [Eqns.(1) and (2)] in comparison with the contribution from the energy of the pair interactions. For such a series of solutions with $\mu_s = \mu_d = 0$ we can expect $|\Delta\nu| \propto E_{disp} - E_{rep}$, whereas with $\mu_s \neq 0$ and $\mu_d = 0$ we have $|\Delta\nu| \propto E_{disp} + E_{ind} - E_{rep}$, and with $\mu_s \neq 0$ and $\mu_d \neq 0$ we have $|\Delta\nu| \propto E_{IMI} = E_{disp} + E_{ind} + E_{or} - E_{rep}$.

Since at ordinary temperatures and pressures the $\bar{R}_{d,s}$ values averaged over the whole volume vary between 5 and 8 Å, the contribution from E_{rep} to the IMI energy is negligible in comparison to that from E_{attr}, as confirmed by the small values of $\Delta\nu$ for many vibrators even at relatively high pressures[31]. If $E_{rep} \ll E_{attr}$ we can expect that in a series of solutions of a non-polar substance in non-polar solvents of the same type

$$|\Delta\nu| \propto E_{disp}. \qquad (3)$$

In the case of solutions of a polar substance in a series of non-polar solvents

$$|\Delta\nu| \propto E_{attr} = E_{disp} + E_{ind}. \qquad (4)$$

On the other hand, for solutions of polar substances in a series of polar solvents of the same type we have

$$|\Delta\nu| \propto E_{attr} = E_{disp} + E_{ind} + E_{or}. \qquad (5)$$

2. Effect of Intermolecular Interactions in Solutions on the Vibration Frequency of Functional Groups in Molecules

Expressions of the type of (3)–(5) have been used[34] to interpret data on ν_{max} for the stretching vibrations of different groups of polar or non-polar molecules. In that work the E_{attr} value (as a function of the molecular properties and of characteristics of the molecular structure

of the solution such as $\bar{Z}$ and $\bar{R}_{s,d}$) was fitted to a London–Debye–Keesom potential for condensed media[35,36]:

$$E_{attr} = \overline{const} \cdot \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \left[\frac{3}{2}\frac{I_s I_d}{I_s + I_d}\alpha_s\alpha_d + \mu_s^2\alpha_d + \mu_s^2\alpha_s + \frac{2\mu_s^2\mu_d^2}{3kT}\right].$$

In studies of the behaviour of a single vibrator in a series of solvents of the same type we can write

$$|\Delta\nu| \propto \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \left[\frac{3}{2}\frac{I_s I_d}{I_s + I_d}\alpha_s\alpha_d + \mu_s^2\alpha_d + \mu_d^2\alpha_s + \frac{2\mu_s^2\mu_d^2}{3kT}\right]. \quad (6)$$

By using Eqn.(6) we can recognise special features in the dependence of $\Delta\nu$ on the characteristics of the solution ($\bar{Z}$ and $\bar{R}_{s,d}$) and on the properties of the vibrator molecule and of the solvent molecule (μ, α, I). It follows from Eqn.(6) that for a given non-polar substance ($\mu_d = 0$) dissolved in a series of non-polar solvents ($\mu_s = 0$) having similar values of I_s we can write

$$\Delta\nu_s \propto C_1 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \alpha_s \qquad \left(C_1 = \frac{3}{2}\frac{I_s I_d}{I_s + I_d}\right)\alpha_d. \quad (7)$$

For a polar solute ($\mu_d \neq 0$)

$$\Delta\nu_s \propto C_2 \sum_k \left(\frac{\bar{Z}}{\bar{R}_{s,d}}\right)_k \alpha_s \quad (C_2 = C_1 + \mu_d^2). \quad (8)$$

In a series of non-polar solvents with similar values of I_s and α_s and T = const. containing a single non-polar solute ($\mu_d = 0$) we have

$$\Delta\nu_s \propto C_1 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \alpha_s + C_3 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \mu_s^2 \quad (C_3 = \alpha_d). \quad (9)$$

For a polar solute

$$\Delta\nu_s \propto C_2 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \alpha_s + C_4 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \mu_s^2 \quad \left(C_4 = \alpha_d + \frac{2}{3kT}\mu_d^2\right). \quad (10)$$

In these expressions C_i are quantities whose variation in a series is slight in comparison to that of the quantities under the summation sign.

We have tested[37] Eqns.(7)–(10) by measuring the ν(C–Cl) absorption for CCl_4 and $\nu(OH)_{free}$ for ethanol in polar and in non-polar solvents. Our results (Fig.1) show that, as required by Eqns.(7)–(10), the ν(C–Cl) and $\nu(OH)_{free}$ values decrease almost linearly with the parameter

$$Y \equiv \bar{Z}\frac{I_s I_d}{I_s + I_d}\frac{\alpha_s}{\bar{R}^6_{s,d}}$$ (i.e. that $\Delta\nu = \nu_s - \nu_{vap}$ increases with Y). This is confirmed by a large amount of published work. For many non-polar solvents of this type the ratios $\bar{Z}I_s/(I_s + I_d)$ and $\alpha_s/\bar{R}^6_{s,d}$ vary in the same sense: this also explains the often reported correlation between $\Delta\nu$ (or ν) and the $\alpha_s/\bar{R}^6_{s,d}$ value in a series of solvents[29,39,40]. The existence of this correlation is confirmed by the large deviation from the straight-line plot of ν or $\Delta\nu$ observed (point 6 in Fig.1) when H-bonded complexes or charge transfer complexes can be formed between the solute molecules and those of the non-polar solvent[41].

Dispersion and inductive interaction can cause a large decrease in ν_s, often of the same order as in polar solvents, which cannot form complexes with solute molecules[40,41]. A large contribution from inductive interactions in the case of polar vibrators in non-polar solvents can be recognised by comparing the $\Delta\nu$ values of the same vibrator for compounds of different polarity in the same non-polar solvents[22,31]. In the case of solvents which cause large deviations from Eqns.(7) and (8) we can calculate the contribution from complex formation or $\pi-\pi$ interaction of the solute and solvent molecules. On the other hand, a study of the contributions from dispersion and inductive IMI has shown that CCl_4 and CS_2 molecules do not take part in complex formation with molecules containing A–H groups[42,49].

The validity of these expressions for intermediate values of α_s, $\bar{Z}_s$, and $\bar{R}_{s,d}$ suggests a volume (as opposed to a local) mechanism for the interaction between molecules in solutions of this type. A volume mechanism can also explain the fact that the $\Delta\nu$ values in non-polar solvents having different but relatively small molecules all lie approximately on the same straight line. Similarly, the strong temperature and pressure dependence of the dispersion and inductive interactions is also consistent with a volume mechanism. An increase in temperature produces a large increase in $R_{s,d}$, and therefore a decrease in $\Delta\nu$.[44] An increase in pressure has the opposite effect on $\Delta\nu$.[31]

In a series of polar solvents with similar values of I_s and α_s (Fig.2) the $|\Delta\nu_s|$ values increase almost linearly with $\bar{Z}\mu_s^2/\bar{R}^6_{s,d}$, as required by Eqns.(9) and (10).

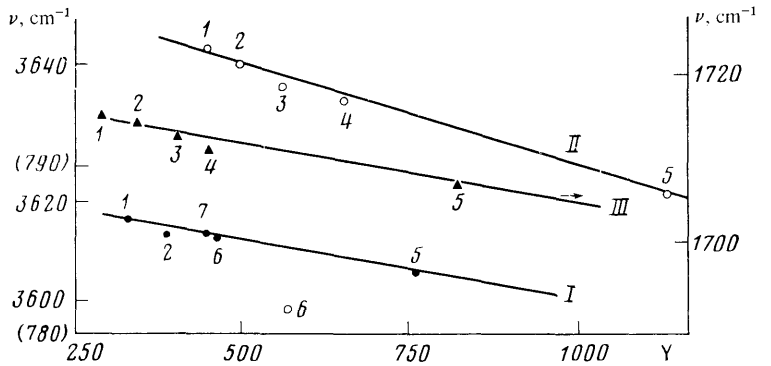


Figure 1. Dependence of ν(C–Cl) on $Y = \bar{Z}\frac{I_s I_d}{I_s + I_d}\frac{\alpha_s}{\bar{R}^6_{s,d}}$ for CCl_4 (*I*), and dependence of ν(O–H) for ethanol[37] (*II*) and of ν(C=O) for benzaldehyde[44] (*III*) in non-polar solvents: *1*) hexane, *2*) cyclohexane, *3*) CCl_4, *4*) C_2Cl_4, *5*) carbon disulphide, *6*) benzene, *7*) dioxan.

An analysis of the above expressions has revealed the following features of the field-induced (dipole–dipole and inductive) interaction of molecules in solutions (in comparison to the specific interactions accompanying the formation of complexes by the same molecules):

a) $|\Delta\nu_S|$ is usually smaller than the usual values for specific interaction between a vibrator molecule and a solvent;

b) the dipole–dipole interaction effect can take place even when the access of the solvent molecules to the proton-donor A–H group is blocked by steric hindrance;

c) the dependence of $|\Delta\nu_S|$ on the chemical composition and structure of the solvent molecules is different from (and almost opposite to) the effects observed during the specific interaction of a vibrator with a solvent[45]. For example, dipole–dipole interaction causes a decrease in $|\Delta\nu_S|$ rather than the increase expected from the decreasing *s*-character of the orbitals of the heteroatom in the solvent molecule [$CH_3CN > C_5H_5N > (C_2H_5)_3N$; $(CH_3)_2C{=}O > (C_2H_5)_2O$]. For solvents which include elements from the same period as heteroatoms, $|\Delta\nu_S|$ decreases in the following sequence: $RCN > RNO_2 > R_2CO > R_2O > R_3N$, which is the inverse of the series describing the tendency of solvents to form H-bonded complexes;

d) in the case of large differences in the size and nature of the solvent molecules (from both the aromatic and the aliphatic series) the $|\Delta\nu_S|$ values for a given vibrator lie on different straight lines if the interaction is of the dipole–dipole type;

e) if the solvent molecules are complex (with several polar functional groups) the $|\Delta\nu_S|$ values are determined by the molecule as a whole rather than by individual dipole moments or by the moment of the most polar group.

3. Effect of the Medium on the Vibrational Spectra of Molecules with Intramolecular and Intermolecular Hydrogen Bonds

In ternary systems [solvent, RAH, and BR', including the RAH...BR' complexes (K)] the vibrational spectra of the A–H group (which forms intermolecular hydrogen bonds) are affected both by changing the solvent and by changing the $c_{BR'}/c_{RAH}$ ratio[16,17,35]. The type of change is not very different from that of a vibrator not involved in hydrogen bond formation. The calculation of these solvent effects merely in terms of macroscopic characteristics such as ε and n,[47–49], or by using empirical relationships[16,46], has been criticised by several workers[2,47,50,51]. One of us[38] has examined the possibility of calculating the effect of the medium on the properties of the A–H group (involved in complex formation) by assuming proportionality (in the case of solvents of the BR' type with similar values of I_S and α_S) between $\Delta\nu_S$ and the parameter $\bar{Z}\mu^2_{BR}/\bar{R}^6_{K,BR'}$, which reflects the change in dipole–dipole interaction of the complex K with the excess of BR' molecules[37,45,52]. The proton-acceptor solvents BR' are chosen so that the changes in $\bar{Z}\alpha_S/\bar{R}^6_{S,d}$ are much smaller than those in $\bar{Z}\mu^2_S/\bar{R}^6_{S,d}$.

An analysis of the absorption spectra revealed the following features in the influence of the medium on the properties of the A–H group in H-bonded complexes. In relation to ν_{max} and $\Delta\nu_{1/2}$ the effect of the medium is relatively unimportant (as compared with the formation of the hydrogen bond itself). On changing from low-polarity ($\mu_{BR'} \leq 1.2$ D) to high-polarity solvents ($\mu_{BR'} > 1.2$ D) the sign of $\Delta\nu_{max}$ changes from positive to negative, and that of $\Delta\nu_{1/2}$ changes in the opposite sense[37]. We should note that when $\mu_{BR'} > 1.2$ D the effect of the medium on all the absorption characteristics is the same as the effect of complex formation. Under these conditions $\Delta\nu_S$(OH) for the complex is always much greater than $\Delta\nu_S$ for the free molecule.

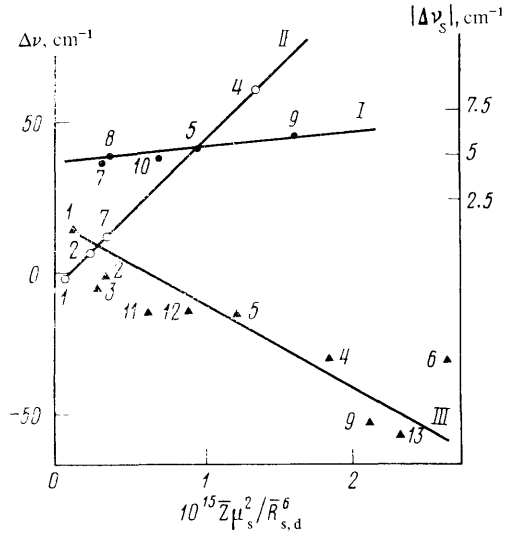


Figure 2. Plots of $\Delta\nu = \nu_{CCl_4} - \nu_{BR'}$ for CCl_4 (*I*), $\Delta\nu$(OH) for *o*-nitrophenol (*II*), and $\Delta\nu = \nu_{BR'} - \nu_{CCl_4+BR'}$ for ethanol (*III*) against $\bar{Z}\mu^2_S/\bar{R}^6_{S,d}$ in polar solvents[37]: *1*) $(C_2H_5)_2O$, *2*) C_4H_9Cl, *3*) $CH_3COOC_2H_5$, *4*) CH_3NO_2, *5*) $(CH_3)_2CO$, *6*) CH_3CN, *7*) CH_3COOCH_3, *8*) $HCOOC_2H_5$, *9*) $HCON(CH_3)_2$, *10*) CH_3COCl, *11*) $HCOOCH_3$, *12*) $CH_3COC_2H_5$, *13*) $(CH_3)_2SO$.

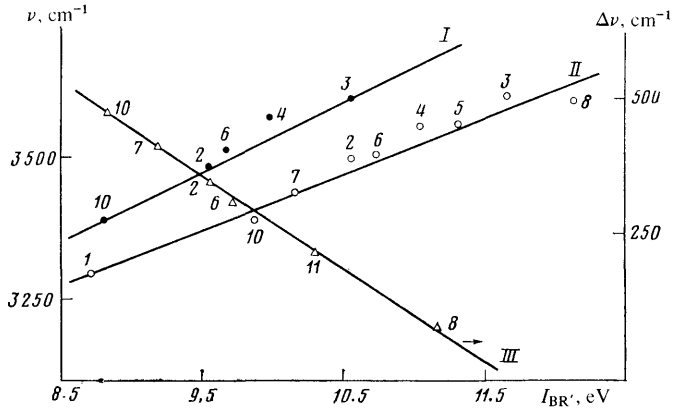


Figure 3. Plots (against the ionisation potential) of the ν(OH) values for ethanol in the ternary ($C_2H_5OH + CCl_4 + BR'$) system (*I*) and in the binary ($C_2H_5OH + BR'$) system (*II*), and of $\Delta\nu_S(OH) = \nu_{CCl_4} - \nu_{BR'}$ for *p*-nitrophenol (*III*),[37] where BR' is: *1*) $(C_2H_5)_3N$, *2*) $(C_2H_5)_2O$, *3*) $n\text{-}C_4H_9Cl$, *4*) $HCOOCH_3$, *5*) $CH_3COOC_2H_5$, *6*) $(CH_3)_2CO$, *7*) $HCON(CH_3)_2$, *8*) CH_3NO_2, *9*) CH_3CN, *10*) $(CH_3)_2SO$.

The ν_{max} (or $\Delta\nu_{max} = \nu(OH)_{free} - \nu(OH)_{h.b.}$] values for the ν(OH) band in the complexes of ethanol and *p*-nitrophenol with BR′ are inversely proportional to $I_{BR'}$ (Fig. 3), as required by the electronic model of the hydrogen bond[38]. The only exceptions are molecules with a proton-accepting power much lower than that of ethanol and a large dipole moment (for example, CH_3NO_2 and CH_3CN). On the other hand, the $\Delta\nu(OH) = \nu(OH)_{bin} - \nu(OH)_{tern}$ values are almost linearly related to $\overline{Z}\mu^2_{BR'}/\overline{R}^6_{RAH,BR'}$, a parameter which characterises the dipole–dipole interaction between the BR′ molecules and the complex (Fig. 2). This justifies the assumption that the main contribution to the change in vibrational frequency caused (for high values of $c_{BR'}/c_{RAH}$) by the displacement of surrounding molecules of non-polar CCl_4 by molecules of polar BR′ comes from the increased dipole–dipole interaction between the complex and the medium.

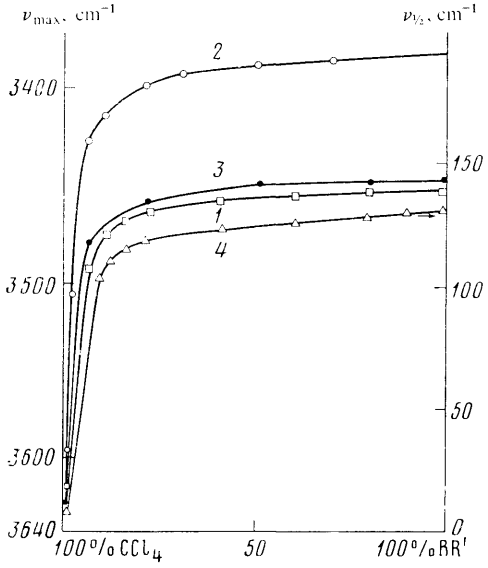
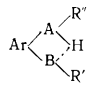


Figure 4. Spectral characteristic ν_{max} of the ν(OH) band against the solvent concentration ratio[37] for *1*) ethanol [BR′ = HCON$(CH_3)_2$]; *2*) ethanol [BR′ = $(CH_3)_2$SO]; *3*) *p*-nitrophenol (BR′ = CH_3NO_2); *4*) is the $\nu_{1/2}$ value of the ν(OH) band of phenol (BR′ = CH_3CN).

In ternary systems the dependence of ν_{max} on $\overline{Z}\mu^2_{BR'}/\overline{R}^6_{RAH,BR'}$ (and hence, for a given value of $\mu_{BR'}$, on $\overline{Z}$ and on $\overline{R}_{RAH,BR'}$) follows from the nature of the change in the spectral characteristics with $c_{BR'}/c_{CCl_4}$.[53–55] The steep increase of ν_{max} (Fig. 4, from Ref. 38) at low values of the ratio $c_{BR'}/c_{CCl_4}$ is due to the formation of a complex with BR′. The more gradual change in ν_{max} is due to the increase in Z caused by the replacement of molecules of non-polar solvent from the first coordination sphere of the complex by excess molecules of the polar compound BR′. The subsequent, even slower, change in ν_{max} is ascribed to the interaction of the complex with BR′ molecules from the outer coordination spheres, for which the interaction energy is very low (because of the large increase in $\overline{R}_{s,d}$).

The spectra due to the formation of intramolecular hydrogen bonds in compounds such as



(where Ar is an aryl group, and R′ and R″ are other parts of the molecule, attached to the atoms A and B) differ in several ways in the ν_s(A–H) absorption region from the spectra corresponding to the formation of an intermolecular hydrogen bond by the *para*-isomer[56,57]. For *o*-nitrophenol[58] and *o*-nitroacetanilide[54] these features are observed also in the effect of the medium on ν_{max} for ν_s(A–H) band of the intramolecular hydrogen bond. In different polar solvents of the BR′ type the ν_{max} value for this band increases in the opposite sense to the normal sequence for the ν_s(A–H) band of the intermolecular hydrogen bond. In solvents having a high proton-accepting power we find an additional band whose maximum usually lies at frequencies higher than the maximum of the ν_s(A–H) band for the intermolecular hydrogen bond[54,58–60].

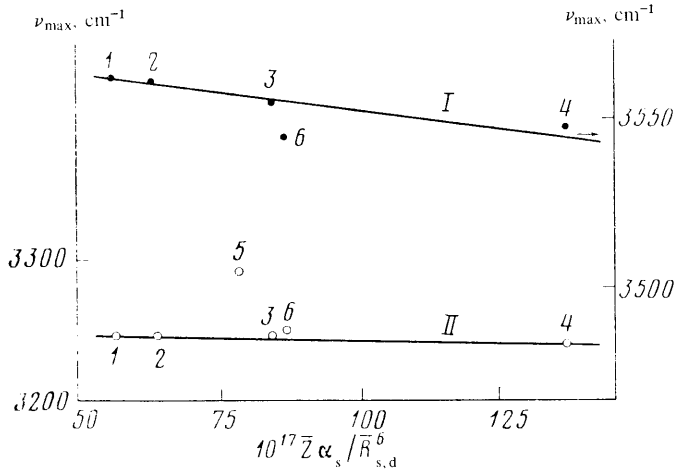


Figure 5. Plots against $\overline{Z}\alpha_s/\overline{R}^6_{s,d}$ of ν_{max} for the ν(OH) bands of guaiacol (*I*) and of *o*-nitrophenol (*II*) in non-polar solvents; *1*) hexane, *2*) cyclohexane, *3*) CCl_4, *4*) hydrogen sulphide, *5*) dioxan, *6*) benzene[58].

These effects of the medium have not yet been fully explained. Some workers[59,60] ascribe them to the breaking of an intramolecular hydrogen bond, with formation of complexes with molecules of the solvent, while others[61] postulate a three-particle complex with a forked hydrogen bond. Some published papers[62,63] explain the increase in ν_{max} in compounds with intramolecular hydrogen bonds in terms of dipole–dipole interactions, which lift the BR′ group from the plane of the aryl ring or displace the bridging proton. In an attempt to solve the problem more strictly[38], the spectral behaviour of molecules with intramolecular or intermolecular hydrogen bonds, and of molecules with a strong or a weak intramolecular hydrogen bond, has been compared as a function of $c_{BR'}/c_{CCl_4}$. The difference $\Delta\nu_{max} = \nu_{CCl_4} - \nu_{BR'}$ was found to increase with the

dispersion interaction energy[64]. This is confirmed by the fact that ν_{max} has about the same dependence on $\overline{Z}\alpha_s/\overline{R}^6_{s,d}$ as $\nu(OH)_{free}$ (see Fig.5, from Ref.38). In ternary systems containing *o*-nitrophenol only the $\nu_s(OH)$ intramolecular hydrogen bond band is observed. The high stability of this bond in *o*-nitrophenol is shown by the slight increase in $\nu_{max}(OH)$ caused by small additions of strong proton acceptors, followed by a steep fall, whereas additions of weak proton acceptors produce a continuous increase in ν_{max} towards the value for the pure BR′ compound (Fig.6),[38] i.e. the strong proton acceptors can break the intramolecular hydrogen bond and displace the equilibrium towards the formation of complexes involving intermolecular hydrogen bonds. On the other hand the increase in ν_{max} for the (A–H) band of the intramolecular hydrogen bond is probably due to non-specific interactions between molecules which contain intramolecular hydrogen bonds and the surrounding medium[65].

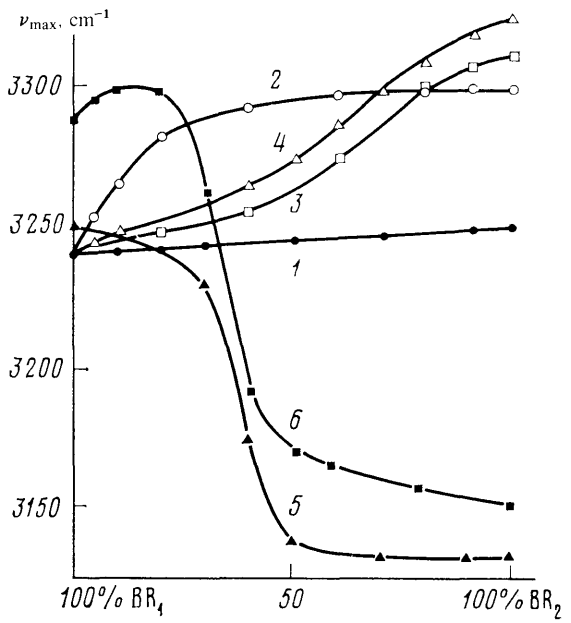


Figure 6. Plots of ν_{max} of the ν(OH) band for *o*-nitrophenol against the solvent concentration ratio (c_{BR_1}/c_{BR_2}) in ternary systems of the *o*-nitrophenol + BR_1 + BR_2 type. The BR_1 + BR_2 combinations are: *1*) CCl_4 + n-C_4H_9Cl, *2*) CCl_4 + CH_3NO_2, *3*) CCl_4 + CH_3CN, *4*) CCl_4 + $CH_3COC_2H_5$, *5*) n-C_4H_9Cl + $(CH_3)_2SO$, *6*) CH_3NO_2 + $(CH_3)_2SO$.[63]

III. INTERMOLECULAR FIELD INTERACTION AND THE CHEMICAL SHIFT OF PROTON SIGNALS

Ever since the first report of its use in studies of the hydrogen bond[66] the proton magnetic resonance (PMR) method has been one of the most useful and successful means of identifying and characterising intermolecular interactions. This is because the PMR spectra reflect both the nature and the extent of the participation of a proton in various interactions. The quantity δ_H (the chemical shift of the signal from hydrogen nuclei) in the PMR spectrum is determined to a first approximation by three independent factors[67]: the state of the electron shell surrounding a particular H atom (i.e. its shape and size), the effect of the surrounding atoms and functional groups in the molecule, and the effect of different kinds of IMI. Thus the quantity δ_H is defined by the structure of the molecule, by the interaction between atoms and functional groups within the molecule, and by the interaction with neighbouring molecules in a pure liquid or in a solution.

The change from the gaseous to the condensed state causes large changes in δ_H(A–H), where A = O, H, C, S. etc. The increment $\Delta\delta_H$(A–H) caused by the medium can be divided into five independent contributions[68–71]:

$$\Delta\delta_H(A\cdots H) = \delta_{vol} + \delta_{an} + \delta_{disp} + \delta_{pol} + \delta_{sp}. \qquad (11)$$

where δ_{vol} is the contribution from the volume susceptibility of the sample, δ_{an} is that due to the non-zero average anisotropy of the magnetic susceptibility of the solvent molecules, δ_{disp} is due to the dispersion interactions between solute molecules and solvent molecules, δ_{pol} is due to polarisation interaction between the molecules, and δ_{sp} is the contribution from specific interactions between molecules of the solvent and of the solute.

Most of the PMR studies of intermolecular interaction published so far are aimed at the contribution δ_{sp}, for two reasons: 1) this contribution is by far the largest, and 2) it can potentially give information on the genesis of intermolecular complexes involving a redistribution of electron density, which are currently of great interest. Since in most cases δ_{sp} is greater than the combined contribution from the other terms in Eqn.(11) it is not unusual to find the whole of the shift $\Delta\delta_H$ caused by the solvent ascribed to intermolecular association effects, the non-specific (field) interaction between solute and solvent molecules being completely ignored.

It is difficult to isolate one of the terms in Eqn.(11) for special study, even with carefully chosen series of solutes and solvents. If the change in volume susceptibility (and hence in δ_{vol}) is allowed for, and the contributions δ_{an} and δ_{sp} can be ignored, the observed increment $\Delta\delta_H$(A–H) should be determined only by field interactions of the molecules (dispersion effects, δ_{disp}, and polarisation effects, δ_{pol}).[67]

The quantity δ_{disp} is determined by two effects[67]: a) the interaction between molecules of the solute and of the solvent causes a loosening of the electron cloud surrounding the nuclei of the solute molecules, leading to a decrease in the diamagnetic screening effect (long-range interaction), and b) the interaction can perturb the symmetry of the electron clouds in the solute molecule (in the *s*-state), giving rise to a paramagnetic contribution in the screening constant (short-range interaction, temperature-dependent).

A quantum-mechanical calculation of the effect of dispersion interaction on the screening constant of the hydrogen atom has shown[72] that van der Waals forces lower the screening and shift the signals towards lower fields. Experimental measurements of the contribution δ_{disp} involve some serious difficulties. The direct method of isolating the contribution δ_{disp} involves comparing the δ_H values for a series of structurally similar non-polar compounds in the gas state and dissolved in non-polar isotropic solvents[82,83]. However, in practice the NMR spectroscopy of gaseous samples is far from straightforward.

To calculate the contribution of dispersion interaction to the magnetic screening of protons in solutions several models have been proposed: the "continuous" dielectric model, the lattice model, and the statistical model. Theoretical calculations of the contribution of the constant G_{disp} to δ_{disp} are also very difficult. The "excess" chemical shifts in the spectra of liquid systems consisting of magnetically isotropic molecules were first explained[74] in terms of dispersion forces. The model developed in that work[74] gives

$$G_{disp} = -\frac{3B\alpha_2 I_2}{2R^6} \qquad (12)$$

where B is the bond parameter ($B = 0.74 \times 10^{-18}$ for the hydrogen atom[75]), and α_2 and I_2 are the polarisability and the ionisation potential of the perturbing solvent molecule.

The "continuous dielectric" model, proposed earlier by Linder[77] for determining the potential energy of the dispersion interaction in pure liquids, has also been used in these calculations[76]. Starting from experimental values of the shift caused by the interaction in a solution of the solute 1 in the solvent 2 (at infinite dilution) Howard and coworkers[76] arrived at the expression

$$G_{disp} = -\frac{3B(2n^2-2)h\nu_1\nu_2}{4(2n^2+1)a^3(\nu_1+\nu_2)} \qquad (13)$$

where n is the refractive index of the solvent, a is the radius of the solute molecule, and $h\nu$ is the excitation energy. A similar model was used in Ref.73. The "continuous" dielectric model led to the conclusion[76] that the contribution of G_{disp} can be described by the expression

$$G_{disp} = -6\left[\frac{(n_2^2-1)^2}{(2n_2^2+1)(n_2^2+2)}\right]_{soln.} \cdot \left[\frac{K_1 B\Delta E_1}{\alpha_1}\right]_{solute}$$

where ΔE_1 is the energy of formation of the transition complex, which can be equated to twice the ionisation potential of this complex, and K_1 is a factor determined by the location of the proton and depending on the geometry of the solute molecule. However, in experimental tests of the expressions for δ_{disp} based on collective interaction concepts[73,74,76] the theoretical values of G_{disp} were inconsistent with measured values.

Calculations of G_{disp} by the "continuous" dielectric model rely on measurements of the characteristic frequencies of the solvent and of the solute (ν_1 and ν_2). These frequencies can be obtained by the formula $\nu = I/h$, which follows from the London approximation[78], where I is the ionisation potential of the molecules. Another formula for calculating the characteristic frequency[77,79] is

$$\nu = -4m_e c^2 \chi_m / hN\alpha \qquad (14)$$

where m_e is the mass of the electron, c is the velocity of light, N is Avogadro's number, α is the polarisability, and χ is the molar susceptibility of the molecules. Lastly, the characteristic frequencies have been calculated[80] by the Lorentz–Lorenz formula for the refractive index.

A calculation of G_{disp} for a large number of systems[81] has given very different results for given systems, depending on the method used to determine ν. A rational choice of the preferred method of calculation among those used in Ref.81 cannot yet be made. It has been suggested[82] that the influence of the medium on the chemical bond arises from the interaction of a solute molecule with the nearest molecules of the solvent "lattice", i.e. that $G_{disp} = Z \cdot G_{disp}(pair)$, where Z is the number of nearest solvent molecules in the "lattice" and $G_{disp}(pair) = -3B\alpha_2 I_2/R^6$ (by analogy with the formula given in Ref.74). The parameter Z was obtained[82] by dividing the area of a sphere passing through the centres of the molecules in the first coordination sphere $[4\pi(r_1+r_2)^2]$ by the effective cross-sectional area of the solvent molecules $(2r_2)^2$. Putting $R = r_1 + r_2$ we find

$$G_{disp} = -\frac{3\pi B\alpha_2 I_2}{(r_1+r_2)^4 r_2^2} \qquad (15)$$

where r_1 and r_2 are the radii of the solute and solvent molecules respectively.

With a suitable choice of series of compounds this model gives δ_{disp} values in good agreement with experiment: however, the results are less reliable when the same approach is used for molecules differing in size, shape, or chemical composition. Better agreement with experiment was obtained[86] by introducing into the formula the factor S_6^g, determined by the location of the resonating proton, and the additional empirical factor K_6^c, depending on the temperature and on the configuration of the solvent and solute molecules:

$$G_{disp} = -K_6^c \frac{3\pi B\alpha_2 I_2}{(r_1+r_2)^4 r_2^3} S_6^g .$$

An alternative approach was developed[83] by studying the effect of the medium in gaseous systems. The contribution from G_{disp} was calculated[83] in terms of binary collisions between the molecules only. The average contribution to the chemical shift from dispersion interactions was determined by using the Lennard-Jones intermolecular potential, and the following formula was obtained:

$$G_{disp} = -\frac{\pi NB\alpha_2 I_2 H_6(X)}{V_2 r_0^3 X^4} \qquad (16)$$

where V_2 is the molar volume of the solvent, $H_6(X)$ is a function tabulated in Ref.84 [$X = 2(\varepsilon/kT)^{1/2}$], ε/kT and r_0 are the force constants in the Lennard-Jones potential, and N is Avogadro's number.

The method[83] is essentially a semi-empirical statistical method, which has proved successful when applied to gases and gas solutions. Other workers[85,86] applied it to liquids, and obtained an expression not very different from (16). However, the model is relatively crude. Firstly, the calculated G_{disp} values are in qualitative rather than quantitative agreement with experiment, even when empirical coefficients are added to the formula. Secondly, the model cannot distinguish between the solvent effects on chemically non-equivalent protons in complex solvent molecules. The theory of pair collisions in gases was later modified[86] in order to apply it to liquids. The van der Waals interaction field $\langle\overline{E}^2\rangle$ near the peripheral protons of the solute molecule was shown to be different from the $\langle\overline{E}^2\rangle$ value at the centre of the molecule, and a correction to allow for the position of the proton in the molecule was added to the formula. The possibility of introducing a term for the repulsive effects into the expression for G_{disp} was examined, but the correction was found to be negligible. The formula finally proposed to describe quantitatively the contribution of dispersion interaction to the chemical shift also includes a temperature factor, to allow for the temperature dependence of G_{disp}:

$$G_{disp} = -(1.46 \pm 0.0064t)\cdot 1.36 \cdot 10^6 \frac{\alpha_2 I_2 H_6(X)}{V_2 r_0^3 X^4} S_6^g . \qquad (17)$$

The parameters S_6^g and $H_6(X)/X^4$ are tabulated in Ref.86. The physical nature of the temperature factor is not stated. Experimental tests of Eqn.(17) were on the whole satisfactory.

In a study[87–90] of various contributions from the medium to the chemical shift a linear combination of terms (including one due to dispersion interaction) was used to express the

chemical shift. The dispersion term was written as a product of contributions from the solvent and the solute respectively. By using this method the authors were able to determine experimentally the G_{disp} contribution for a number of systems. The experimental results were compared with theoretical calculations by the formulae of the collective interaction model[76,77], or by a formula obtained[85,86] from the statistical theory of pair collisions. The agreement in both cases was surprisingly good, and a critical analysis of the two methods of calculating G_{disp} was thought unnecessary.

The two sets of calculations (Refs.76, 77 and 85, 86), though differing in detail, have a great deal in common. First of all they both rely on generalised collective parameters, and therefore they cannot be used to study the dependence of δ_{disp} on the microscopic parameters of the interacting molecules. In spite of its relative success in calculations of G_{disp}, formula (17) (which was obtained from the theory of pair collisions in gases) has a number of shortcomings. The model is not applicable to large molecules, which require replacement of the one-centre Lennard-Jones potential by a many-centre potential force field. This is a serious limitation of all the models discussed above, especially in the case of aromatic solvents. The reliance on physical constants which are not always available creates further obstacles to the use of this working formula. Thus, though G_{disp} values have been successfully calculated, the method is not suitable for day-to-day use in the laboratory.

Allowance for polarisation effects is needed when one of the components of the solution is polar. This contribution is usually small[113], and can be described by the formula

$$\delta_{pol} = \delta_{disp} \frac{2\mu_2^2}{3\alpha_2 I_2}$$

where μ_2 is the (constant) dipole moment, α_2 is the polarisability, and I_2 is the ionisation potential of the solvent molecule. However, for small solvent molecules with large dipole moments the contribution from δ_{pol} becomes comparable to δ_{disp}.[103] An approximate calculation[60] has shown that for a proton of the A–H group the screening component associated with the external electric field is $\sigma_E = -AE_z - BE^2$, where A and B are constants and E_z is the component of the electric field E in a direction parallel to the A–H bond. The shift of the proton signal caused by the electric field is explained by the repulsion experienced by the excess charge on the proton, which lowers the electron density on the 1s orbital of the hydrogen and the screening constant[91]. Furthermore, the presence of an electric field hinders the diamagnetic current circulation within the hydrogen atom, which again lowers the screening constant and shifts the proton signal towards lower fields[92].

A polar molecule added to a solution polarises the surrounding medium, and its nuclei experience the reactive field of the medium. Starting from the Onsager model[14], and identifying E_z with the reaction field, Linder[77] obtained the following formula for δ_{pol}:

$$\delta_{pol} = -\text{const} \cdot \left(\frac{\varepsilon - 1}{2\varepsilon + n^2}\right) \frac{\mu \cos\varphi}{2} \qquad (18)$$

where ϕ is the angle between $\vec{\mu}$ and the C–H bond.

According to formula (18), in a binary solution the solute is characterised by the refractive index n, the dipole moment μ, and the polarisability α, and the solvent is characterised only by one macroscopic property: the dielectric constant ε.

Diehl and Freeman[93] made some improvements in Buckingham's theory to allow for the polar contribution, and proposed a slightly different model, which takes account of the shape of the solute molecule. They arrived at a modified formula for the reaction field, which reduces to the formula given by the Onsager model in the case of spherically symmetrical molecules. However, the expression obtained in Ref.93 is not very different from Eqn.(18). Better correlations have been obtained[94] by using formula (18) for the internal (or relative) shift between two non-equivalent protons in a molecule rather than for the chemical shift of any one proton. This should allow all effects to be excluded except the reaction field effects. This assertion was tested[95] with a series of methyl-substituted nitrobenzenes in 13 different solvents. It was found that only by limiting the choice of solvents to those having carefully chosen properties could good correlations be obtained with experimental data on the internal chemical shift, calculated by the reaction field theory based on the Onsager model.

If the polar component is the solvent, the influence of the electrostatic field created by its dipoles on the solute molecule is almost equivalent to the reaction field calculated by Buckingham[68], whose linear effect causes a change in the polarity of the A–H bond. It is clear from formula (18) that solutions of a polar solute in a series of solvents having different ε values should be described by the expression

$$\Delta\delta_H(\text{A}-\text{H}) \sim \frac{\varepsilon - 1}{2\varepsilon + n^2} \cdot \qquad (19)$$

However, expressions for the polar contribution to the chemical shift of protons in a solute molecule in terms of the macroscopic properties of the solution[68,96,97] are not precise enough for use in PMR.

In many polar (and in some non-polar) solvents the chemical shifts are very different from those calculated by formulae such as (19). Thus, according to Buckingham[68] solvents like n-hexane, nitromethane, acetonitrile, and acetaldehyde do not follow the correlation (19); carbon tetrachloride, acetone, acetonitrile, etc.[97], and dimethylsulphoxide, *N*,*N*-dimethylformamide, etc.[98,99] are also found to behave abnormally. On the other hand, as a result of the use of generalised properties of the components in these correlations it is impossible to study directly the dependence of the chemical shift $\Delta\delta_H$(A–H) on the physical properties and on the structure of the solute and solvent molecules and on the different types of intermolecular interaction. This led to various attempts to relate the $\Delta\delta_H$(A–H) values to other properties of the components, such as the polarity constant of the solvents[96], the dipole moment of the solute molecules μ_d,[98–100] the ratio of the dipole moment to the molar volume μ_d/V,[69] etc.

The calculation of the effect of dispersion and polarisation field interactions on the chemical shift of protons in the interacting molecules has also been examined from a different aspect[101]. A physically more justifiable set of equations was obtained[101] by assuming proportionality between the chemical shift due to field interactions and the energy of the pair interactions between the solute and the solvent molecules ($\Delta\delta_{field} \propto |U_{s,d}|_{pair}$). The parameter $|U_{s,d}|$ was calculated in the dipole approximation[8]: $|U_{s,d}|_{pair} = |E_{s,d}|_{disp} + |E_{s,d}|_{pol} + |E_{s,d}|_{el.st.}$, using the London, Debye, and Keesom potentials respectively for the additive contributions to the energy. In the case of dilute solutions, when the solute molecules are surrounded by solvent molecules only and no local interactions take place through the overlap of electron clouds, we can write[8]

$$\Delta(\delta_{disp} + \delta_{pol}) \propto |U_{s,d}|_{pair} = \frac{1}{R^6_{s,d}} \left\{ \frac{3}{2} \frac{I_s I_d}{I_s + I_d} \alpha_s \alpha_d + \mu_s^2 \alpha_d + \mu_d^2 \alpha_s + \frac{2}{3} \frac{\mu_s^2 \mu_d^2}{kT} \right\}. \qquad (20)$$

Formula (20) has a number of advantages over those given above. It shows explicitly the relationship between the chemical shift due to field interactions and the microscopic properties of the interacting molecules. The expression contains one of the most important parameters of IMI: the distance between the interacting molecules, which does not appear in formulae based on Onsager concepts. Furthermore formula (20) suggests a suitable methodology for studying the dependence of $\Delta\delta_{H,field}$ on molecular properties: by the strict selection of series of compounds related by particular characteristics. Thus, it follows from Eqn.(20) that the expression

$$\Delta(\delta_{11})_{disp} \sim \alpha_s/\bar{R}^3_{s,d} \qquad (21)$$

can be applied to solutions of a given non-polar substance ($\mu_d = 0$) in a series of non-polar solvents ($\mu_S = 0$) with similar values of I_S (i.e. in the presence of dispersion interaction only between molecules of the components).

Similar relationships apply to the chemical shifts of solutions of a given polar substance in a series of non-polar solvents with similar values of I_S, and also to solutions in a given non-polar solvent of a series of polar substances for which μ_d = const but with widely different values of α_S. For solutions of a given non-polar or polar substance in a series of polar solvents with similar values of I_S, α_S, and $\bar{R}_S$ (a condition easily satisfied by isoperiodic solvents with molecules of similar shape) we find the correlation[101,102]

$$\Delta\delta_{11}(A-H) \sim \mu_1^2/\bar{R}^6_{s,d} \qquad (22)$$

or, for a series of solvents selected more critically in respect of molar volume and molecular shape, we find the expression

$$\Delta\delta_{11}(A-H) \sim \mu_s^2 \ . \qquad (23)$$

These expressions have been tested[102] against a large amount of experimental information from different laboratories. Many data for δ_H(A–H) are quoted[102], but only for A=C (ring protons, protons in CH_3 groups, etc.) does comparison between calculation and result confirm the validity of Eqns.(21)–(23) when applied to different series of binary solutions of aromatic or aliphatic compounds. Calculation of δ_{disp} and δ_{pol} by Eqn.(20) shows that δ_H(C–H) is determined by interactions between solute and solvent molecules which are not local in character but are averaged over all possible orientations of the interacting molecules. Under these conditions the proton can become unscreened either as a result of proton withdrawal effects due to the electric field or as a result of the displacement towards the carbon atom of the electrons in the C–H σ-bond, also due to the electric field[83]. The change in the charge on the carbon atom[104] due to the redistribution of the electron density in the remainder of the molecule (other than the C–H group) under the influence of the field may also have a part to play.

A field interaction (of the volume type) with the surrounding molecules may also explain the change in the spectra of complexes in solution[102]. As Fig.7 (taken from Ref.102) shows, the change in the chemical shift of the bridging proton signal in the spectra of phenol and chloroform complexes with the proton acceptor BR′ caused by interaction with the medium is linearly related to the parameter $\bar{Z}_S\mu_S^2/\bar{R}^6_{S,d}$ (except in the case of very weak proton acceptors). This relationship also accounts for the change in chemical shift caused by varying the ratio of the concentrations of the proton acceptor solvent (BR′) and of the non-polar solvent in ternary systems (Fig.8, from Ref.102).

Thus the London, Debye, and Keesom potentials for pair interactions of the field type between component molecules can be used to calculate the effect of the solvent on the magnitude and direction of the chemical shift of the proton signal in solutions where complex formation cannot take place.

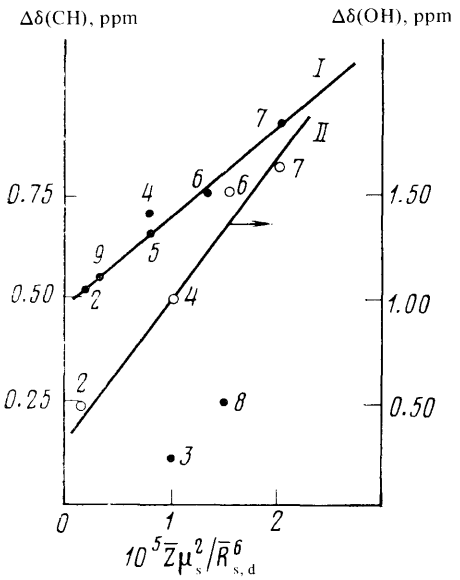


Figure 7. Plots of $\Delta\delta_H = (\delta_H)_{BR'} - (\delta_H)_{CCl_4+BR'}$ against $\bar{Z}\mu_S^2/\bar{R}^6_{S,d}$ for δ(CH) of chloroform (*I*) and δ(OH) of phenol (*II*) and different BR′: *1*) CCl_4, *2*) $(C_2H_5)_2O$, *3*) n-C_4H_9Cl, *4*) $(CD_3)_2CO$, *5*) $CH_3COC_2H_5$, *6*) $HCON(CH_3)_2$, *7*) $(CD_3)_2SO$, *8*) CH_3NO_2, *9*) $CH_3COOC_2H_5$.[102]

IV. EFFECT OF THE SOLVENT ON THE BASIC CHARACTERISTICS OF THE ELECTRONIC SPECTRA OF MOLECULES

1. Comparison of Methods of Calculating the Effect of the Medium on the Electronic Spectra of Molecules

Several studies of the influence of solvents on the basic characteristics (ν_{max} and the oscillator strength *f*) of the electronic spectra of molecules have been reported[105–109]. The parameter ν_{max} is usually obtained from universal expressions in terms of the generalised properties of the solvent *n* and ε.[2,108].

Bayliss[110] proposed the concept of a "general red shift", determined by the interaction with the medium of the dipole moment associated with the transition of the molecule. The shift $\Delta\nu$ is given by the formula

$$\Delta\nu = -cf\frac{n^2-1}{2n^2+1} \ , \qquad (24)$$

where *f* is the oscillator strength of the band, *c* is a constant, and *n* is the refractive index of the solvent.

Bayliss and Rae[111], using the Franck–Condon principle, arrived at a general scheme describing the effect of the solvent on electronic absorption spectra which allows

(qualitatively) for the main types of IMI. According to this treatment the displacement of the absorption band of a compound in solution relative to the spectrum of the same compound in the vapour phase is due to the difference between the energy of the interaction with the surroundings of the molecule in the ground and in the excited electronic state. Under these conditions the stabilisation energy for different electronic levels should be determined in each particular case in terms of the nature of the interaction between the molecule under study and the solvent molecules.

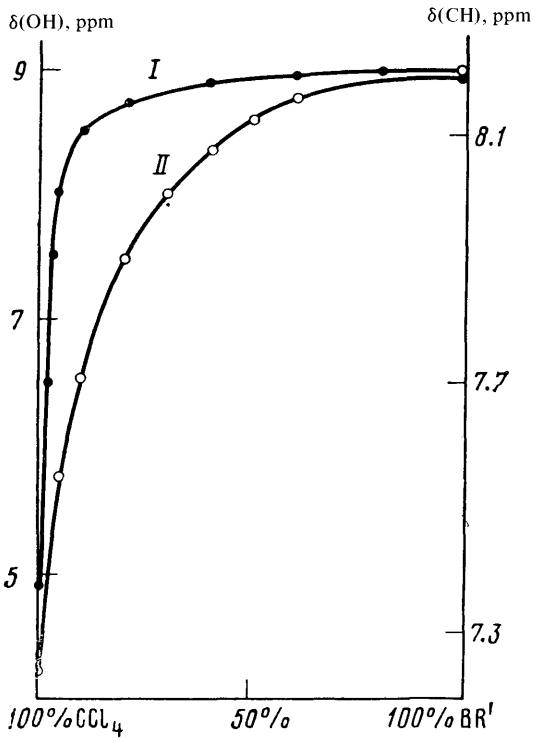


Figure 8. Plots of δ_H for the δ(OH) band of phenol (*I*) and of δ(CH) for chloroform (*II*) against the concentration ratio of CCl_4 and BR' [BR' = $(CD_3)_2CO$ for (*I*) and $HCON(CH_3)_2$ for (*II*)].[102]

An attempt has been made[112] to calculate the stabilisation energy of the electronic levels of molecules in solutions by assuming IMI of the dipolar type only. The stabilisation energies of the various levels were calculated from the basic characteristics of the interacting molecules, allowing for the changes in some of these characteristics caused by the absorption of a light quantum. The shift in the spectrum is treated essentially as due to the statistical averaging of the set of interactions between the solute molecule and the nearest-neighbour solvent molecules, and quantitative expressions are obtained by using the Onsager model.

A theoretical discussion[113] of the effect of the solvent on fluorescence spectra has shown that in general the shifts in the absorption and the emission band of any molecule undergoing a phase transition should be different. Two explanations are suggested: firstly, that the configuration of the solvent molecules around the solute molecule is different for solute molecules in the ground and in the excited state, and secondly that this configuration is not changed by the electronic transition (as required by the Franck–Condon principle).

A theoretical analysis of the effect of dipole–dipole interactions on the frequency of bands in the electronic spectra of solutions is given in Ref. 114. A simple electrostatic model yields expressions relating the frequency shifts in absorption and emission spectra to the parameters n and ε of the solvent. A theory of the effect of van der Waals interactions on the electronic spectra of molecules has been developed[115] from both semi-classical and quantum-mechanical foundations: the two approaches give qualitatively consistent results.

Important advances have been made in the application of computers to the analysis of experimental results[113–119]. The use of Kosower's Z parameter[119], an empirical characteristic of the polarity of the medium or (according to Kosower[119]) a microscopic measure of the type and strength of the interaction between solute and solvent molecules, has given interesting results in the analysis of experimental data on band shifts in electronic spectra. The same author has developed a method of determining the H-bond energy and the dipole moment in the excited state from absorption spectra by using the Z parameters.

The current state of spectroscopic research on intermolecular interactions has been systematically reviewed by Bakhshiev[2], who also showed[120] that intermolecular interactions in condensed media can affect, in general, not only all the physicochemical properties of the molecule of interest but also the field strength associated with a light wave acting on the molecule and inducing transitions between energy levels. He derived a general expression for the change in integral intensity of a band caused by the transfer of the molecule from the gas to the condensed state, which includes the correction factor $\bar{\theta}_\uparrow$ to allow for all the effects of the difference in field strength of the light wave between the condensed medium and a vacuum.

The first attempt to determine the form of the factor $\bar{\theta}_\uparrow$ by using the Lorentz model gave an expression[121] (applicable to dilute solutions) of the form

$$\bar{\theta}_\uparrow = 9n/(n^2+2)^2 \,. \qquad (25)$$

On the other hand, by using the Onsager model the following expression was obtained[131] for $\bar{\theta}_\uparrow$:

$$\bar{\theta}_\uparrow = n\left(\frac{2n^2-1}{3n^2}\right)^2 . \qquad (26)$$

The following formula was also obtained[123]:

$$\bar{\theta}_\uparrow = \frac{(2n^2+1)^2}{9n^3}\left(1-\frac{\bar{\alpha}}{a}\frac{2n^2-2}{2n^2+2}\right)^2 , \qquad (27)$$

where $\bar{\alpha}$ is the mean value of the real part of the complex polarisability of the molecule of interest, and a is the Onsager radius of the molecule.

A quantitative theory of the shift in electronic bands produced by universal intermolecular interactions is developed in Bakhshiev's papers, with full allowance for the different types of IMI. According to Bakhshiev the contribution from universal IMI is given by the formula $\Delta\nu^0 = C_1^a F(\varepsilon,n)$, where C_1^a is a characteristic of the properties of the solute molecule, and the universal interaction function $F(\varepsilon,n)$ characterises mainly the properties of the solvent. The function

$$F(\varepsilon,n) = \left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n_D^2-1}{n_D^2+2}\right)\frac{2n^2+1}{n^2+2} + P\frac{n^2-1}{n^2+2} \equiv A + PB \qquad (28)$$

is determined by the dielectric constant ε and the refractive index of the solvent (n_D for the visible region of the spectrum and n for the spectral region which includes the band of interest). The parameter P depends mainly on the change in polarisability of the solute molecule caused by the electronic excitation.

This method has been used[124,125] to separate the contributions ($\Delta\nu^0$) of the universal IMI from those ($\Delta\nu$) due to the formation of intermolecular hydrogen bonds (the $n \to \pi^*$ absorption bands of some aliphatic ketones). Though the Onsager model yields relatively simple expressions, readily tested experimentally[2,108], in both the quantum-mechanical and the classical approach, its application has been shown[126] to be severely limited. In addition to the well-known approximations implicit in the Onsager model, the Stark effect is ignored in the universal functions, and the parameter which characterises the size of the hole in the liquid structure is not expressed with adequate precision. Therefore the universal functions $f(\varepsilon)$, $f(n)$ and $f(\varepsilon,n)$, which rely on the generalised properties of the solvent, depend also on a number of features of both the solution structure and the various types of IMI.

Because of this, the effect of solvents on the ν_{00} value of absorption bands has been studied[126] by the model of pair interactions between molecules. The resulting expression explicitly includes the role of one of the most important factors in IMI: the distance between solvent and solute molecules. The expression is

$$\Delta\nu = \nu_s - \nu_{vap} = \frac{\bar{Z}\bar{\varphi}}{\bar{R}^6_{s,d}}\left\{\frac{3}{2}\left(\frac{I_d^{FC}\alpha_d^{FC}}{I_s^{gr}+I_d^{FC}} - \frac{\alpha_d^{gr}I_d^{gr}}{I_s^{gr}+I_d^{gr}}\right) I_s^{gr}\alpha_s^{gr} + [(\mu_d^{FC})^2 - \right.$$
$$\left. -(\mu_d^{gr})^2]\alpha_s^{gr} + [\mu_s^2(\alpha_d^{FC}-\alpha_d^{gr})] + \frac{2}{3kT}[\mu_d^{gr}\mu_d^{FC}\cos\beta - (\mu_d^{gr})^2]\mu_s^2\right\}, \quad (29)$$

where $\bar{\varphi}$ is a correction for non-additivity of the pair interactions and for the inaccuracy of the expressions for the various contributions to the potential, the superscripts "gr" and "FC" denote parameters of the ground state and the Franck–Condon state respectively, and β is the angle between the vectors $\vec{\mu}^{gr}$ and $\vec{\mu}^{FC}$.

For a given non-polar or polar solute undergoing a given electronic transition in a series of non-polar solvents the following expression was obtained[126]:

$$\Delta\nu = \bar{Z}\bar{\varphi}\left\{\left[\left(\frac{A}{I_s^{gr}+I_d^{FC}} - \frac{B}{I_s^{gr}+I_d^{gr}}\right)+C\right]\frac{\alpha_s}{\bar{R}^6_{s,d}}\right\}, \quad (30)$$

and for a series of polar solvents

$$\Delta\nu = \bar{Z}\bar{\varphi}\left\{\left[\left(\frac{A}{I_s^{gr}+I_d^{FC}} - \frac{B}{I_s^{gr}+I_d^{gr}}\right)-C\right]\frac{\alpha_s}{\bar{R}^6_{s,d}} + D\,\frac{\mu_s^2}{\bar{R}^6_{s,d}}\right\}, \quad (31)$$

where A, B, C, and D are constants. If the I_s^{gr} values are similar, if the product $\bar{Z}\bar{\varphi}$ is constant, and if no complexes are formed between molecules of the components, we find $\Delta\nu \propto \alpha_s/\bar{R}^6_{s,d}$ in the case of non-polar solvents, whereas in polar solvents with similar values of $\bar{R}_{s,d}$ and α_s but relatively large differences in μ_s we find $\Delta\nu \propto \mu_s^2/\bar{R}^6_{s,d}$ (or even $\Delta\nu \propto \mu_s^2$).

Many workers have tried to establish a relationship between the intensity of the absorption band and the solvent effect[126–130]. Thus, Chako proposed a formula[127] based on the classical theory of dispersion interaction which sets out the relation between f_s and f_{vap} but does not take account of the properties of the solute molecule:

$$\frac{f_s}{f_{vap}} = \frac{(n^2+2)^2}{9n^2}. \quad (32)$$

The changes in the field of the light wave in the dielectric have also been studied in detail by the Onsager model by Schleyer[128], who proposed a method of calculating the ratio of the molar extinction coefficients for the solution and the gaseous state. Abe[130] obtained the following expression:

$$\frac{f_s}{f_{vap}} = \frac{(n^2+2)^2}{9n^2}\,\frac{E_s}{E_{vap}}, \quad (33)$$

(where E is the energy of the transition), based on the Onsager model, which takes account of not only the effect of the solvent but also the properties of the solute molecule.

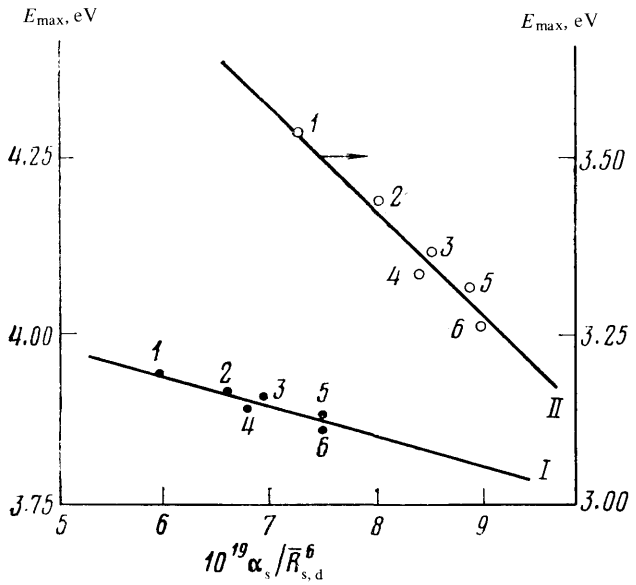


Figure 9. Plots against $\alpha_S/\bar{R}^6_{S,d}$ of the E_{max} values of the bands for the $\pi^* \leftarrow \pi$ transition in azobenzene (*I*) and the $\pi^*_{NO_2} \leftarrow n_{N(CH_3)_2}$ transition in *p*-nitrodimethylaniline (*II*). Solvents: *1*) hexane, *2*) cyclohexane, *3*) CCl_4, *4*) *p*-xylene, *5*) mesitylene, *6*) benzene[132].

2. Effect of Field Interactions on the Characteristic Absorption Bands of Substituted Benzenes

The effect of field interactions between solvent and solute molecules has been studied[131,132] in order to test the expressions (28)–(31). Fig.9 (from Ref.132) shows the dependence of E_{max} on $\alpha_S/\bar{R}^6_{S,d}$ for a number of substances. In the series of non-polar solvents the variation (increase) of E_{max} with $\alpha_S/\bar{R}^6_{S,d}$ is almost linear, both for the $\pi^* \leftarrow \pi$ band of the transition in azobenzene and for the $\pi^* \leftarrow n$ charge transfer bands of the other aromatic compounds. Fig.10 (from Ref.133) shows plots of E_{max} against $\mu_S^2/\bar{R}^6_{S,d}$ for two solutes in a series of polar solvents having the same (or similar) numbers of atoms of elements from the same period. In this case E_{max} decreases linearly with $\mu_S^2/\bar{R}^6_{S,d}$.

Thus we may conclude that the interaction between solute and solvent molecules is of the field type, i.e. that dispersion, dipole–dipole, and inductive interactions take place between the molecules. The contribution from inductive interaction in non-polar solvents depends on the difference in dipole moments, and in the case of polar solvents it depends also on the difference in polarisability of the solute molecules in the Franck–Condon and in the ground state.

Some special features of the effect of solvents on the oscillator strength f of the absorption bands of a range of compounds have been pointed out[132]. Starting from the formula (given in Ref.130) $f_S/f_{vap} = \frac{(n^2+2)^2}{9n^2}\frac{E_S}{E_{vap}}$ we find that for a given electronic transition in a solute molecule in a non-polar solvent $f = \text{const}\,\frac{(n^2+2)^2}{9n^2}E_{S,max}$. Fig.11 shows that this expression is reasonably well-obeyed. In Fig.12 (from Ref.132) we note that the parameter f decreases almost linearly with increase in $\alpha_S/\bar{R}^6_{S,d}$ in non-polar solvents.

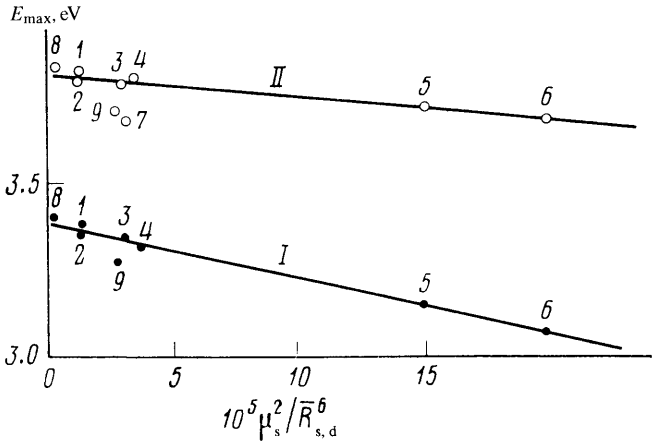


Figure 10. Plots against $\mu_S^2/\bar{R}^6_{S,d}$ of the E_{max} values of the bands for the $\pi^*_{NO_2} \leftarrow n_{N(CH_3)_2}$ transition in *p*-nitrodimethylaniline (*I*) and the $\pi^*_{CHO} \leftarrow n_{N(CH_3)_2}$ transition in *p*-dimethylaminobenzaldehyde (*II*). Solvents: *1*) $(C_2H_5)_2O$, *2*) $(C_2H_5)_2NH$, *3*) $n\text{-}C_4H_9Cl$, *4*) CH_3COOCH_3, *5*) $HCON(CH_3)_2$, *6*) $(CH_3)_2SO$, *7*) $iso\text{-}C_3H_7OH$, *8*) $N(C_2H_5)_3$, *9*) $n\text{-}C_3H_7OH$.[132]

3. Intermolecular Interaction with Hydrogen Bond Formation

The electronic spectra of H-bonded complexes are discussed in several papers, but the type and extent of the influence of complex formation on the electronic spectra (or, more exactly, on the E_{max} and f values) are not yet fully understood. From the fact that ΔE_{max} (and $\Delta\nu_{max}$) are described by the universal functions $f(\varepsilon)$ and $f(\varepsilon,n)$ [134,135] some workers conclude that specific interactions are weak, or absent, in the electronic spectra of compounds forming complexes with a solvent[2]. The main contribution to ΔE_{max} during complex formation has been ascribed[136–139] to the difference in energy of the hydrogen bond in the ground and the excited state. However, a more widely held view[140,141] is that E_{max} under these conditions is equal to the sum of two contributions: the van der Waals interaction and the ΔE_2 value for the formation of the hydrogen bond, and either of these contributions can be predominant under suitable conditions. Attempted calculations of these contributions in terms of universal functions[124,125] yielded functions which proved both cumbersome and inaccurate. Because of the approximations implicit in the derivation of universal functions based on the Onsager model, and because the interaction with solvent molecules affects the complex as a whole (and not the separate molecule of solute[64]), the influence of the solvent on hydrogen-bonded complexes has been studied[133] in terms of the potentials of pair interactions between the molecules[126].

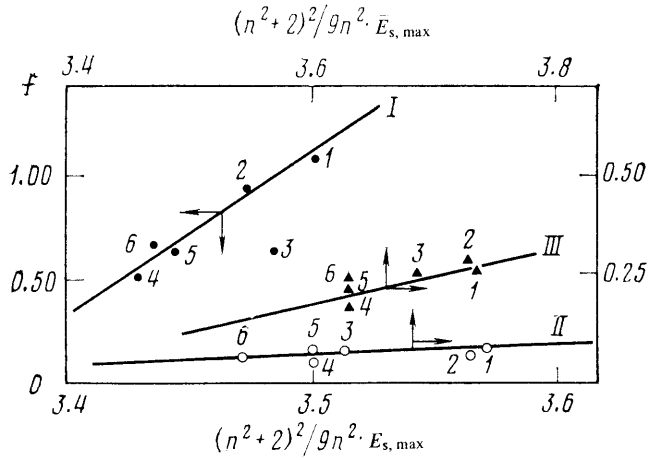


Figure 11. Plots of f against $(n^2+2)^2/9n^2 \cdot E_{max}$ for the absorption bands of azobenzene (*I*), *o*-nitroanisole (*II*), and *p*-nitroanisole (*III*). Solvents: *1*) n-hexane, *2*) cyclohexane, *3*) CCl_4, *4*) *p*-xylene, *5*) mesitylene, *6*) benzene[132].

Both in compounds which contain no proton-donor groups and in compounds able to form hydrogen-bonded complexes the E_{max} value decreases linearly with $\alpha_S/\bar{R}^6_{S,d}$ in non-polar solvents, and with $\mu_S^2/\bar{R}^6_{S,d}$ in polar solvents. This suggests that the predominant contribution to the solvent effect in the formation of the intermolecular hydrogen bond comes from ΔE_1 rather than from ΔE_2. Methods of calculating the separate contributions to ΔE_{max} from ΔE_1 and ΔE_2 have been suggested[132].

4. Effect of Solvents on the Electronic Spectra of Molecules with Conjugated Chains of Different Length

The optical absorption of these compounds has been studied in a large number of solvents[142,143]. Kuhn and Schweig[144] have calculated the shifts in the absorption and fluorescence bands of polar molecules of organic dyes under the influence of solvents. We have examined[145] the dependence of E_{max} (for the absorption bands) on $\alpha_S/\bar{R}^6_{S,d}$ and $\mu_S^2/\bar{R}^6_{S,d}$ in a series of compounds with conjugated chains of different length of the NO_2ZNR_2 type (where Z is an aryl group containing different numbers of π bonds).

The E_{max} value of the long-wave band with appreciable charge transfer, of the $\pi^*_{NO_2} \leftarrow n_{NR_2}$ type, was exactly described by the proposed expression[145] in every case, whatever the size of the solute molecule: it decreases linearly as the parameter $\alpha_S/\bar{R}^6_{S,d}$ increased. In polar

solvents also the E_{max} value of both absorption bands decreases as $\mu_S^2/\bar{R}_{S,d}^6$ increases. As the number of π bonds in the aromatic ring increases, the E_{max} value decreases almost linearly, and the slope of the linear plots increases slightly. For all the NO_2ZNR_2 compounds examined in polar solvents the dependence of f on $\mu_S^2/\bar{R}_{S,d}^6$ (produced by varying the size of the group Z) was accurately linear.

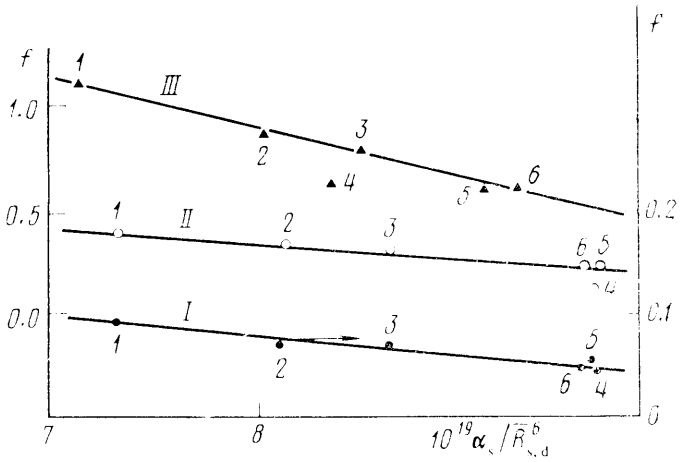


Figure 12. Plots against $\alpha_S/\bar{R}_{S,d}^6$ of the parameter f for the absorption bands of *o*-nitroanisole (*I*), *p*-nitroanisole (*II*), and *p*-dimethylaminobenzaldehyde (*III*). Solvents: *1*) n-hexane, *2*) cyclohexane, *3*) CCl_4, *4*) *p*-xylene, *5*) mesitylene, *6*) benzene[132].

Thus in a series of non-polar solvents with similar values of the ionisation potential the difference in the effect of the solvent on ν_{max} is due to $\alpha_S/\bar{R}_{S,d}^6$, whereas in polar solvents with similar values of $\bar{R}_{S,d}$ and α_S it is due to the parameter $\mu_S^2/\bar{R}_{S,d}^6$.

We have shown that the effect of intermolecular interactions in solutions on the spectral characteristics of molecules can be calculated by using the London–Debye–Keesom pair interaction potential for condensed media. The main advantage of this method is that it leads to expressions for the interaction energy containing in an explicit form the molecular properties of both the solute and the solvent (dipole moment, ionisation potential, polarisability) as well as parameters which characterise the molecular structure of the solution (Z and $\bar{R}_{S,d}$).

The expressions apply both to compounds which do not form hydrogen bonds and experience only intermolecular interactions of the field type and to compounds able to form hydrogen bonds with the solvent.

We have also shown that the relative contributions to the intermolecular interaction energy from field interaction effects and from complex formation by hydrogen bonds can be calculated approximately.

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Surface Ionisation of Organic Compounds

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The equilibrium thermal emission of positive ions of organic compounds from the surfaces of heated solids is examined. The possibilities of employing this phenomenon in the physical and analytical chemistry of organic compounds are illustrated.
The bibliography includes 75 references.

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I. INTRODUCTION

Surface ionisation (SI) consists of the formation of ions in the course of the thermal desorption of species from the surface of a solid. In the general case surface ionisation includes three consecutive stages: the arrival of the species on the surface; the establishment of thermal and charge equilibria between the adsorbed species and the solid; evaporation of the species from the surface of the solid. In the last stage the single solid–species system breaks up into two subsystems over distances from the solid (x_{cr}) of the order of magnitude of atomic dimensions and the final charge state of the desorbed species is established. It depends on the probability of the isoenergetic electron exchange between the species and the solid. In a simplified form, this is illustrated in Fig.1: the species can become a positive ion if its valence electron can occupy a vacant level in the solid; conversely, if the electron of the solid can pass to a vacant orbital of the species, the latter can be desorbed in the form of a negative ion.

Surface ionisation was discovered by Langmuir and Kingdon in 1923:[1] a current comprising positive ions passed through a vacuum diode with an incandescent tungsten wire when caesium vapour was admitted. Langmuir and Kingdon obtained an expression for the degree of surface ionisation of atoms α within a closed uniform metallic cavity at a temperature T (Kingdon and Langmuir[2]) (the Saha–Langmuir formula):

$$\alpha = A \exp[e(\varphi - V)/kT], \quad (1)$$

where $\alpha = n^+/n^0$ is the ratio of the equilibrium concentrations of the ions and atoms within the cavity, A the ratio of

the statistical weights of the ionic and neutral states of the atoms ($A = 1/2$ in the case of Cs), $e\phi$ the electron work function of the wall of the cavity, V the ionisation potential of caesium, k the Boltzmann constant, and e the electronic charge.

It was established in subsequent years that positive atomic ions of the majority of elements and the negative ions of many elements can be obtained by surface ionisation. Ion sources for different purposes and detectors of atomic fluxes have been devised on the basis of surface ionisation. A general theory of the phenomenon has been developed. It describes the formation of positive and negative ions on ionisation of the atoms of any elements, not only within closed cavities but also on open surfaces which are both uniform and non-uniform as regards emission; the influence on α of external electric fields, which accelerate ions, has been examined.

The most complete theory of the phenomenon is described in a monograph[3]. It is based on the ideas of statistical thermodynamics and leads to explicit expressions for the current densities in different cases of ionisation. The possibility of the experimental determination of the parameters in these expressions from the measured current has become the basis of the development of a new application of surface ionisation—its employment as a method for the physicochemical investigation of many properties of solids, ionisable atoms, and the characteristics of the interaction of atoms with a solid.

More than twenty such methods have been developed recently, in particular, those for the determination of ionisation potentials, electron affinities, the lifetimes of atoms and ions on the surface, the heats of desorption of atoms and ions, and the emission characteristics of solids, for the study of phase transitions in adsorbed layers, for the determination of the activities of catalysts in heterogeneous dissociation reactions, etc.[3-5]. Evidently the surface ionisation of molecules, radicals, and complexes can yield valuable information about the properties of these species and also about their interaction with a solid.

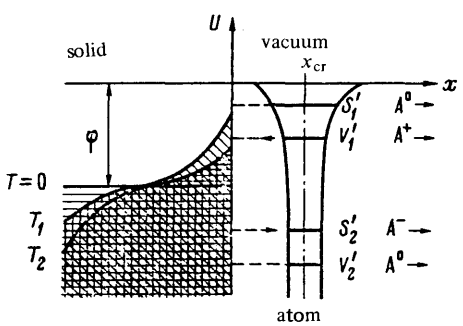


Figure 1. Illustration of the charge state of the desorbed species; $T < T_1 < T_2$.

Experimental studies on the surface ionisation of organic compounds (polyatomic species) have been begun recently. The possibility of the thermal desorption of organic ions was first indicated in studies carried out towards the end of the 1950's and the beginning of the 1960's;[6-10] some of these yielded elaborate mass spectra of the ions obtained on ionisation of the residual gases and vapours in the mass spectrometer[8-10], which can be accounted for only by the ionisation of organic compounds, for example, the vapours of the oils seeping from the pumps. Next, a change in the conductivity of flow-type diodes with an incandescent platinum or a molybdenum anode when specific organic compounds (the vapours of hydrocarbons, alcohols, ethers, and ketones) mixed with air or oxygen at atmospheric pressure were passed through them was observed[11-14]; however, it was not possible to observe the ionisation of the same compounds with the aid of the mass-spectrometric technique[10].

A number of studies on the surface ionisation of organic compounds involving the formation of negative ions have been performed by Page and coworkers using a magnetron technique. A systematic account of these studies has been published[15]; the electron affinities of many molecules and radicals have been determined with the aid of surface ionisation. However, subsequent mass-spectrometric studies established that the composition of the negative ions put forward in Page's studies did not correspond to reality[16,17] and that the ions were most probably formed not by surface ionisation but via some other mechanisms in secondary and tertiary side reactions associated with the emission of thermal electrons from the emitter[17]. Thus certain electron affinities are incorrect and it is regrettable that they are still quoted in the reference literature (for example, by Kondrat'ev[18]).

Systematic studies on the surface ionisation of organic compounds were begun in 1965 at the Ioffe Physicotechnical Institute of the USSR Academy of Sciences. Initially their aim was to discover the classes of organic compounds capable of ionising on heated surfaces. In the course of these studies it was found that, apart from the equilibrium thermal ionisation, non-equilibrium thermal ionisation also occurs, for example, in those cases where the energy evolved on decomposition of the molecule on the surface participates in the ionisation of the fragments[19-21]. Certain organic peroxides ionise in this way; the SI emission relations cannot be used to describe the ionisation of this type. As regards surface ionisation with formation of negative ions, hitherto it has been possible to obtain only the ions of small molecular fragments as a consequence of the small (as a rule) electron affinities of organic molecules and radicals and the requirement that the emitters of ions have high temperatures[17].

Extensive data have already accumulated on the surface ionisation of individual organic compounds with formation of polyatomic positive ions; the classes of ionisable compounds have been found, the principal rules governing the phenomenon have been established, and a number of its applications have been developed. These problems are considered in the present review.

II. CHARACTERISTICS OF THE SURFACE IONISATION OF ORGANIC COMPOUNDS

The theory of surface ionisation does not impose limitations on the composition of the ionising species. These can be polyatomic species, which includes both species incident on the surface and species formed from them as a result of chemical reactions in the adsorbed layer. The only important factor is that thermal and charge equilibria are established on the surface during the lifetime of the species.

If the molecule on the surface of the emitter can be converted into i types of new species, the incident flux of molecules ν can be conveniently represented as one

comprising i effective fluxes ν_i, each of which forms species of only one kind. There is then a relation between ν_i and ν:[22]

$$\nu_i(T, E) = \gamma_i(T, E)\nu, \quad (2)$$

where $\gamma_i(T, E)$ is a coefficient, which depends, for a given molecule–emitter pair, on the emitter temperature T and the electric field strength E at its surface. It defines the concentration of the ith species in the adsorbed layer as a result of all the processes occuring in it[23]. The ionisation of each kind of species can be treated independently of the ionisation of species of another type.

When the ion current is generated on the surface, the ratio of the charged component of the evaporating flux to its uncharged component $\alpha_i = \nu_i^+/\nu_i^0$ is given by the following formula for a surface uniform with respect to the electron work function ϕ in weak electric fields:

$$\alpha_i = A_i \exp\{e[(\varphi - V_i) + (eE)^{1/2}]/kT\}. \quad (3)$$

For polyatomic ith species, V_i is the first adiabatic ionisation potential and $A_i = Q_i^+/Q_i^0$ is the ratio of the total partition functions (translational, rotational, vibrational, nuclear, and electronic) for the charged and neutral species at the temperature T.[20] By definition, $0 < \alpha_i \leq \infty$.

As in the ionisation of atoms, a convenient characteristic is the ionisation coefficient

$$\beta_i = \nu_i^+/\nu_i, \quad (4)$$

which by definition lies in the range $0 \leq \beta_i \leq 1$.

Under steady-state conditions (when the effective flux ν_i is equal to the evaporating flux, i.e. $\nu_i = \nu_i^+ + \nu_i^0$), α_i and β_i are linked by the relation

$$\beta_i = (1 + 1/\alpha_i)^{-1}. \quad (5)$$

The current due to ions of the ith type is

$$I_i = e\nu_i^+ F = e\nu_i\beta_i F = e\nu\gamma_i\beta_i F, \quad (6)$$

where F is the area of the emitting surface. We obtain from Eqns.(3), (5), and (6)

$$I_i = e\nu\gamma_i F \Big/ \left\{1 + \frac{1}{A_i}\exp\left[\frac{e}{kT}(V_i - \varphi - (eE)^{1/2})\right]\right\}, \quad (7)$$

In two cases common in practice Eqn.(7) simplies significantly.

1. The case of difficult ionisation: $e[V_i - \phi - (eE)^{1/2}] \gg kT$. Only a small proportion of the incident species are ionised under these conditions; we obtain from Eqn.(7)

$$I_i \simeq e\nu\gamma_i F A_i \exp\left[\frac{e}{kT}(\varphi + (eE)^{1/2} - V_i)\right]. \quad (8)$$

The relation between I_i and T may be exponential or more complex owing to the relation between γ_i and T.

2. The case of easy ionisation: $e[\phi + (eE)^{1/2} - V_i] \gg kT$. We then obtain from Eqn.(7)

$$I_i(T, E) \simeq e\nu\gamma_i F, \quad (9)$$

i.e. virtually every species produced on the surface ionises.

If the emitter is non-uniform with respect to ϕ (for example, is polycrystalline), then, when the contact potentials of the spots on its surface are compensated by the external electric field (electric field strengths in the range $E \simeq 10^3$–10^4 V cm^{-1} are usually sufficient for this), the ionic current is equal to the sum of the currents from the individual spots. In this case the ionisation within narrow temperature ranges can be represented as occurring on a uniform surface; it is characterised by the effective parameters ϕ^*, A_i^* (Zandberg and Ionov[3]), and γ_i^*. The form of Eqns.(7)–(9) then remains unaltered.

III. EXPERIMENTAL TECHNIQUE

The methods used to investigate the surface ionisation of organic compounds must ensure the following conditions: (1) reliable identification of the ions; (2) the possibility of elucidating the problem of the thermal equilibrium in the adsorbed layer of the species; (3) the application of ion emitters with a high work function (the values of V for organic compounds exceed 7–8 eV [18]), which is stable in time; (4) the possibility of measuring T and ϕ under working conditions.

Special high-vacuum mass-spectrometric devices have been constructed at the Ioffe Physicotechnical Institute for the investigation of the surface ionisation of organic compounds[19,20,24]. The ionic currents due to the thermal ionisation of the vapours of the residual substances are virtually absent in these devices. Vacuum distillation of the substances introduced is used and the surface ionisation and electron ionisation mass spectra are compared at different stages of the distillation process (for this purpose, there is an additional source of ions with electron ionisation). If the sample contains impurities, it is possible to establish by this procedure to which substances the ions obtained refer and this is important in view of the selectivity of the surface ionisation with respect to V: a small amount of impurity with a smaller value of V can mask the current due to the main substance [for example, for two substances with $V_1 > V_2 > \phi$ and $V_1 - V_2 = 2eV$, we obtain from Eqn.(8) $I_2/I_1 \simeq 10^9$ at 1000 K].

The problem of the thermal equilibrium is studied by analysing the energies of the ions on the basis of the normal components of the initial translational velocities[3]. In principle, such analogy is insufficient in the case of polyatomic species, since all types of internal motion in the latter must also correspond to equilibrium. However, one can assume that in the adsorbed layers of the species there is the same sequence in the attainment of equilibrium by different forms of motion as in the gas phase, i.e. that the vibrational processes are slowest[25]. The thermal equilibrium in the translational motion of species indicates equilibrium in their vibrational motion. Since the energy of the bond between the chemisorbed molecules and the solid is of the same order of magnitude as the energy of the bonds between the atoms in the molecule, the equilibrium distribution of ions with respect to kinetic energy may indicate also the attainment of equilibrium with respect to all types of motion of the adsorbed species.

The search for the most effective emitters in order to obtain the ions of organic compounds led to oxidised metals exhibiting a catalytic activity in relation to the dissociation of the molecules and higher values of ϕ.[8,26,27]. Under the influence of organic compounds, the emission properties of oxidised metals vary with time[27], so that, in order to increase their continuous operation time, the vapours of the test substances are admitted only until the attainment of a pressure of approximately 1×10^{-5}–1×10^{-4} Pa. In view of the non-uniformity of the oxidised metals with respect to ϕ,[26,28] provision is made for the measurement under working conditions of both the effective electron work function ϕ_e^* and the effective ion work function ϕ_i^*. A Knudsen cell with a substance difficult to ionise, for example, bismuth ($V = 7.287$ eV) is present in the surface-ionisation ion source in order to measure ϕ_i^*.

At the surface of the emitter the strength of the external electric field $E \simeq 10^3$–10^5 V cm^{-1}, this is sufficient to compensate for the contact fields of the spots but is much smaller than required for the desorption of the ions by the field[29].

The search for substances capable of surface ionisation has been carried out among compounds of different classes. Simple hydrocarbons, alcohols, ethers, ketones, nitrocompounds, and nitriles do not ionise[19,30]. Amines, hydrazines and their various derivatives, phosphines, arsines, and certain oxygen-containing substances (phenols, organic acids, and benzene derivatives) do ionise. Compounds containing Group VA elements, which form polyatomic radicals containing these heteroatoms, ionise with the greatest efficiency.

IV. CHARACTERISTIC FEATURES OF THE FORMATION OF IONS BY ORGANIC COMPOUNDS CONTAINING GROUP VA HETEROATOMS

The surface ionisation of approximately 70 compounds of different classes[30] (mainly the effectively ionisable amines[30-35], hydrazines[36], and their derivatives[34,37,38]) has now been investigated, mainly on emitters consisting of oxidised tungsten[26] and also on tungsten, molybdenum, nickel, rhenium, and iridium, oxidised molybdenum and nickel, and nichrome emitters[27,28,30].

In all cases the initial kinetic energy of translation of the ions desorbed from the surface of the emitter corresponded to equilibrium with the temperature of the emitter[24,31]. The currents due to molecular ions and the ions derived from the dissociation products of the molecules on the surface of the emitter depended linearly on the vapour pressure of the test substance, while the currents due to the associated species $(M + H)^+$, obtained on ionisation of primary and secondary amines and phosphines, depended on the square of the vapour pressure[39].

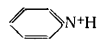
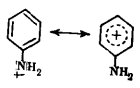
In virtually all publications the surface ionisation mass spectra are presented in the form of tables such as Table 1, where the following parameters are indicated in addition to the mass number m: the maximum ionic current density j (A cm^{-2}) referred to the vapour pressure $p = 1.33 \times 10^{-5}$ Pa, measured with an ionisation gauge calibrated against nitrogen†, the corresponding emitter temperatures, the postulated chemical structures of the ions (for this purpose, the surface ionisation of labelled compounds has been studied in a number of instances[35,36]), and the ionisation potentials of the ionising species estimated by SI methods.

In the ionisation of *alkylamines*[30-33] (the SI mass spectra of which are presented in Table 1), the following features were discovered.

1. The products of the chemical reactions of the molecules of the initial amines (mainly dissociation reactions) ionise on the surface of the emitter and not the molecules of the initial amines themselves.

2. In the SI mass spectra the number of lines is small. They may contain, regardless of the material of the emitter, lines due to ions within the set $(M - H)^+$, $(M - Alk)^+$,

Table 1. The surface-ionisation mass spectra of a series of amines.

Compound	M, a.u.	V_M, V	m_i, a.u.	Ion	j, A cm^{-2}	T, K	Postulated structure of ion	V_i, V	Refs.
Ethylamine	45	8.87 [40]	46	$(M+H)^+$	$3\cdot10^{-14}$	600	$C_2H_5N^+H_3$	$\lesssim$7.8	[32]
			44	$(M-H)^+$	$1\cdot10^{-12}$	1100	$CH_3-CH=N^+H_2$	$\lesssim$8.3	
Diethylamine	73	8.01 [40]	74	$(M+H)^+$	$1\cdot10^{-9}$	550	$(C_2H_5)_2N^+H_2$	$\lesssim$7.2	[32]
			72	$(M-H)^+$	$3\cdot10^{-8}$	700	$CH_3-CH=N^+H-C_2H_5$	$\lesssim$7.2	
			70	$(M-3H)^+$	$1\cdot10^{-9}$	700	$CH_3-CH=N^+H-CH=CH_2$	$\lesssim$7.4	
			58	$(M-CH_3)^+$	$2\cdot10^{-10}$	1100	$CH_2=N^+H-C_2H_5$	$\lesssim$7.8	
Triethylamine	101	7.50 [40]	102	$(M+H)^+$	traces	550	$(C_2H_5)_3N^+H$	—	[32]
			100	$(M-H)^+$	$4\cdot10^{-7}$	600	$(C_2H_5)_2N^+=CH-CH_3$	$\lesssim$6.9	
			98	$(M-3H)^+$	$2\cdot10^{-9}$	600	C_2H_3, C_2H_5 $N^+=CH-CH_3$	—	
			86	$(M-CH_3)^+$	$2.5\cdot10^{-7}$	1150	$(C_2H_5)_2N^+=CH_2$	$\lesssim$7.1	
			84	$(M-CH_3-2H)^+$	$2\cdot10^{-9}$	1150	C_2H_3, C_2H_5 $N^+=CH_2$	—	
n-Pentylamine	87	—	88	$(M+H)^+$	$3.5\cdot10^{-11}$	650	$CH_3(CH_2)_4N^+H_3$	$\lesssim$7.7	[31]
			86	$(M-H)^+$	$7\cdot10^{-10}$	1200	$CH_3(CH_2)_3CH=N^+H_2$	$\lesssim$8.0	
			85	$(M-2H)^+$	$1.5\cdot10^{-11}$	1200	$C_5H_{11}N^+$	—	
			84	$(M-3H)^+$	$2\cdot10^{-10}$	1200	$CH_3-CH_2-CH=CH-CH=N^+H_2$	—	
			83	$(M-4H)^+$	$7\cdot10^{-13}$	1200	$C_5H_9N^+$	—	
			82	$(M-5H)^+$	$7\cdot10^{-12}$	1200	$CH_2=CH-CH=CH-CH=N^+H_2$	—	
			81	$(M-6H)^+$	$7\cdot10^{-13}$	1200	$C_5H_7N^+$	—	
			80	$(M-7H)^+$	$7\cdot10^{-12}$	1200	$C_5H_5N^+H$	—	
Pyridine	79	9.32 [40]	80	$(M+H)^+$	$3\cdot10^{-13}$	550		$\lesssim$7.5	[31]
Aniline	93	7.69 [41]	93	M^+	$3\cdot10^{-11}$	1100		7.65+0.07	[42]

Notation. M is the molecular weight of the substance, V_M its ionisation potential, m_i the mass of the ion, and j the current density.

†In this calibration of the gauge, there is an error in the determination of the vapour pressure p of organic substances resulting in an overestimate. Therefore the values of j presented are correspondingly too low.

$(M + H)^+$, $(M - H - nH)^+$, and $(M - Alk - nH)^+$.

3. As a rule, all the ions formed in the surface ionisation of alkylamines have an even number of electrons and they can be represented as ions containing quadrivalent positively-charged nitrogen atoms with sp^3-, sp^2-, or sp-hybrid orbitals. The current density due to such ions greatly exceeds that of radical-ions.

4. The ionisation potentials of the radicals (M - H) and (M - Alk), as well as the associated species (M + H) are as a rule lower than the V_M for the initial molecules. Therefore if the ions M^+ are in fact formed via surface ionisation under the conditions of the experiment, they cannot be detected against the background of a significantly more intense line due to the isotopic ions of the $m + 1$ radicals (M - H).

5. The current densities of isotypical radical and associated species depend on the nature of the groups attached to the nitrogen atom: the current density increases significantly as the hydrogen atoms in the amino-group are substituted by alkyl groups.

6. The efficiency of the surface ionisation of alkylamines, particularly secondary and tertiary amines, is high. Thus the overall ion current density in the ionisation of tertiary alkylamines on oxidised tungsten reaches approximately 0.1 A Pa^{-1} cm^{-2}, i.e. each 2–5 molecules of the amine arriving on the surface of the emitter lead to the formation of one ion on average.

7. The temperature variations of the ion currents of each species are characteristic (Fig.2), which is due to the difference between the temperature variations of the yields of the reaction involving the formation of ionisable species of each kind; reactions leading to the formation of associated species proceed at lower temperatures than the dissociation reactions; the temperature threshold of the reaction resulting in the formation of the (M - Alk) species is much higher than for the reaction in which the hydrogen atom is abstracted; the threshold ionisation temperatures for the (M + H) and (M - H) species are determined by the threshold surface ionisation temperature[30,39] and those for the (M - Alk) species are determined by the temperature threshold of the reaction[23,30].

8. The species (M + H) are formed on the surface of the emitter as a result of the association of the adsorbed molecules via hydrogen bonding and of the subsequent decomposition of the associated species[39].

The influence of substituents in the molecules of amines on the composition of their SI mass spectra and on the ionisation efficiency has been demonstrated for the SI of trimethylamines of the type $(CH_3)_2N-CH_2-R$, where $R = CH_3$ (I), $CH = CH_2$ (II), $N(CH_3)_2$ (III), CN (IV), C_6H_5 (V), or p-$C_6H_4NO_2$ (VI).[34,35] The SI mass spectra of these substances consist of lines due to the ions $(M - H)^+$ and $(M - R)^+$. The efficiency of the formation of the ions $(M - H)^+$ depends significantly on the electronegativity of the substituent R: the current densities of the ions $(M - H)^+$ vary over five orders of magnitude (from approximately 2×10^{-2} to approximately 2×10^{-7} A Pa^{-1} cm^{-2}) and are qualitatively correlated with the Taft substituent constants.

The radicals (M - R) derived from the above trimethylamines are identical, namely $(CH_3)_2N\dot{C}H_2$; on surface ionisation, they give rise to the stable ions $(CH_3)_2N^+CH_2 \rightleftharpoons (CH_3)_2NC^+H_2$, stabilised by the presence of an unshared electron pair at the nitrogen atom and the electron-donating methyl groups. However, the current densities of the ions derived from these radicals and the form of the relations between j and T for ionisation on the same emitter differ appreciably (Fig.3). This is associated with the difference between the $\gamma-T$ relations. The current density of the ions $(M - R)^+$ produced by tetramethyldiaminomethane ($j \gtrsim 5 \times 10^{-2}$ A Pa^{-1} cm^{-2}) and the absence of a dependence of j on T over a wide temperature range lead to the conclusion that the ionisation potential of this radical $V < \phi_i^*$. Here $\beta \cong 1$ (Zandberg and Ionov[3]) and it follows from Eqn.(9) that the $I-T$ relations in all the remaining cases reproduce the $\gamma-T$ relations, while the ratios of the values of j are the same as the ratios of the γ.

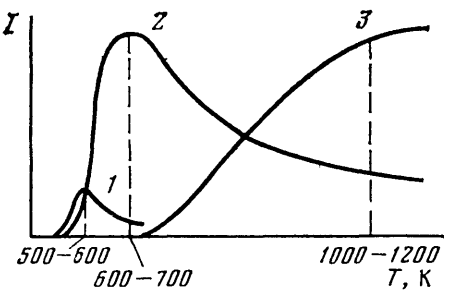


Figure 2. Temperature variation of the currents in the surface ionisation of alkylamines on oxidised tungsten[43]: *1*) $(M + H)^+$ ions; *2*) $(M - H)^+$ ions; *3*) $(M - R)^+$ ions.

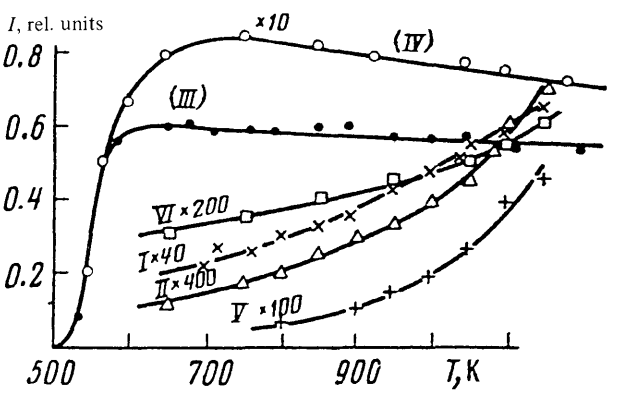


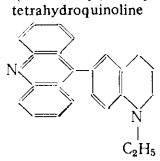
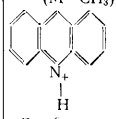
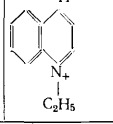
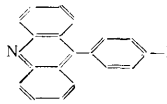
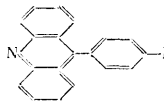
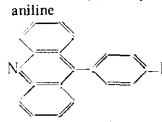
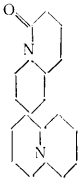
Figure 3. Temperature variation of the currents due to the $(M - R)^+$ ions in the ionisation of the substituted trimethylamines (I)–(VI).[34]

A qualitative correlation between the yield on the emitter of the products of the reactions involving the formation of the radicals (M - R) and the energy of formation of the radical R can be traced. The lower the latter, the higher the current density due to the ions $(M - R)^+$. It is noteworthy that the overall density of the currents due to all the ions in the surface ionisation of substituted trimethylamines is high and changes only slightly on passing from one compound to another. Thus the overall current density is in the range ~10^{-2}–10^{-1} A Pa^{-1} cm^{-2} for compounds (I)–(V).[34]

The ionisation of more complex bases such as acridinyltetrahydroquinolines and acridinylanilines with different substituents at the nitrogen atom, benzimidazoles, the alkaloid allomatrine, etc. (the SI mass spectra of some of these represented in Table 2) obeys the same rules governing

the formation of ions as in the surface ionisation of simple amines[37]; in particular their mass spectra consist of the same characteristic set of lines due to the ions $(M + H)^+$, M^+, $(M - H)^+$, $(M - R)^+$, and $(M - H - 2nH)^+$.

Table 2. The parameters of the mass spectra of certain *N,N*-heterocyclic compounds[37].

Compound	m_i, a.u.	Ion	Relative intensity, %	*T*, K	*j*, A cm-2
6-(9′-Acridinyl)-1-ethyl-1,2,3,4-tetrahydroquinoline 	339	$(M+H)^+$	0.5		—
	338	M^+	4		—
	337	$(M-H)^+$	11		—
	335	$(M-3H)^+$	100	1000	$\sim 5\cdot10^{-8}$ (90)
	323	$(M-CH_3)^+$	1.5		—
	180 		2		—
	158 		10		—
4-(9′-Acridinyl)aniline 	272	$(M+H)^+$	15		—
	271	M^+	100	1150	$2\cdot10^{-11}$ (120)
4-(9′-Acridinyl)dimethyl-aniline 	299	$(M+H)^+$	1		—
	298	M^+	2		—
	297	$(M-H)^+$	100	150	$\sim 2\cdot10^{-10}$ (120)
4-(9′-Acridinyl)diethyl-aniline 	327	$(M+H)^+$	—		—
	326	M^+	1		—
	325	$(M-H)^+$	67		—
	323	$(M-3H)^+$	33		—
	321	$(M-5H)^+$	11		—
	311	$(M-CH_3)^+$	100	1150	$1\cdot10^{-9}$ (100)
Allomatrine 	249	$(M+H)^+$	—		
	247	$(M-H)^+$	75		
	245	$(M-3H)^+$	80		
	243	$(M-5H)^+$	100	1170	$1\cdot10^{-8}$ (25)
	241	$(M-7H)^+$	60		
	239	$(M-9H)^+$	20		
	235	$(M-11H)^+$	10		
	235	$(M-13H)^+$	2		

*The evaporator temperature (°C) is given in brackets.

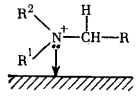
Simple rules for the formation of ions have been formulated on the basis of the analysis of the SI mass spectra of amines and their derivatives whereby one can predict the composition of the ions in the SI mass spectra of the amines and estimate the ion current densities[37,43]. These rules can be accounted for by the high selectivity of the surface ionisation in relation to the ionisation potentials *V* of the ionising species, the favourable energetic features of the formation of ions with saturated bonds, which in the case of amines can be represented by ions with a quadrivalent positively-charged nitrogen atom having hybrid orbitals, and by the dependence of *V* for the ionising species on the electronegativities of the substituents. Thus the ionisation of the amine $R^1R^2N\text{-}CH_2R$ always results in the formation of ions derived from the radicals (M - H) and (M - R), obtained on dissociation of the β-bond (relative to nitrogen) in the adsorbed molecules. The current density of the ions $(M - H)^+$ is determined by the electronegativities of the substituents R^1, R^2, and R. In the case of alkylamines, $j \cong (10^{-6}\text{–}10^{-4})$ for primary amines, $\sim 10^{-3}$ for secondary amines, and $\sim(10^{-2}\text{–}10^{-1})$ A Pa^{-1} cm^{-2} for tertiary amines[30]. The current density of the ions $(M - R)^+$ depends on the electronegativities of the substituents R^1 and R^2 and also on the energy of formation of the radical R. If R^1 and R^2 are alkyl groups, then the current density of the ions $(M - R)^+$ is $\sim(10^{-2}\text{–}10^{-1})$ A Pa^{-1} cm^{-2}.[30,32–34]

The lines due to the ions $(M - H - 2nH)^+$ and $(M - R - 2nH)^+$, which are formed on ionisation of the dehydrogenation products of the molecules on the surfaces of oxidised metals (when metallic emitters are used, these ions are hardly detected), should be observed in the SI mass spectra on ionisation of molecules with alkyl substituents. The intensity of the lines due to these ions on ionisation of amines with linear alkyl substituents is lower than the intensity of the lines of the ions $(M - H)^+$ and $(M - R)^+$ and decreases with increase of *n*. In the mass spectra of alicyclic compounds with the nitrogen atom in the ring, the intensity of the lines due to the ions $(M - H - 2nH)^+$, in which the ring has been aromatised, may be considerable and may increase the intensity of the lines due to the ions $(M - H)^+$.[37]

The lines of the ions $(M + H)^+$, formed on ionisation of the complexes (M + H), should be always present in the SI mass spectra of primary and secondary amines at low temperatures of the emitter; the complexes are obtained as a result of the self-association of the molecules on the surface of the emitter[39]. The ions $(M + H)^+$ can be detected also in the ionisation of tertiary amines; however, in this case the complex formation is due to the presence of polar molecules, for example, H_2O, in the residual gas within the mass spectrometer[32,34].

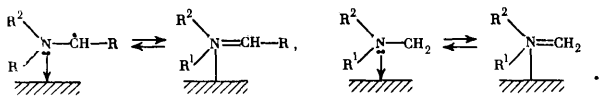
Points due to molecular ions M^+ which are susceptible to measurement can be obtained in those cases where the ionisation potentials of the molecules do not exceed the work function of the emitter by more than approximately 2 eV and during their lifetime in the adsorbed state the molecules must not be fully converted into species of another chemical composition. This happens, for example, in the case of aromatic amines and nitrogen-containing heterocyclic compounds[37,42]. However, even if the above conditions are fulfilled, the lines due to the ions M^+ can be more readily detected, as already mentioned, on ionisation of substances which do not form the ions $(M - H)^+$ effectively.

The rules governing the formation of ions, common to all the amines and their derivatives and independent of the material of the emitter, have been used to elucidate the mechanism of the adsorption of amine molecules and their reactions on the emitter[20,43]. One may conclude that the amines are adsorbed as a result of the formation of a coordinate bond with the adsorbent; the withdrawal of the electron pair to the emitter which occurs under these conditions leads to the formation of a partial positive charge on the nitrogen atom:



This causes a significant weakening of the β-bonds relative to the nitrogen atom[44] and explains the formation of the

radicals (M - H) and (M - R) on the surface of the emitter:



Measurements of the average lifetimes on the surface of the emitter have shown that such species persist on the emitter for a long period[23] (see below), reach thermal and charge equilibrium with the latter, and, on desorption, ionise via the surface ionisation mechanism.

Apart from the reactions examined, other reactions leading to the appearance of both ionising molecular fragments [for example, the products of the dehydration of the molecules—the species (M - H - 2*n*H) and (M - R - 2*n*H)] and non-ionising molecular fragments, can occur on adsorption of amines. However, the high efficiency of the formation of the ions $(M - H)^+$ and $(M - R)^+$ observed in many instances shows that the reactions involving the formation of the species (M - H) and (M -R) on adsorption of amines predominate and can take place with yields close to unity.

The above pattern in the adsorption of amine molecules is supported also by the low threshold temperatures for the ionisation of the radicals (M - H), which are even lower than the threshold temperatures for the ionisation of fluxes of Cs atoms having the same density[23]: if the adsorbed amine molecules were bound to the surface via many atoms, the species would have been desorbed at much higher temperatures.

The study of the surface ionisation of a series of *alkylhydrazines*[30,36] on emitters consisting of oxidised tungsten and molybdenum showed that, although the introduction into the molecule of the second heteroatom with formation of the >N–N< bond leads to some differences in the rules governing the formation of ions compared with amines, for example, it results in the formation of the ions M^+ [as a consequence of the decrease of the values of V_M for the molecules and the mutual approach of the ionisation potentials of the molecules and the radicals (M - H) compared with amines] and to the absence of lines of the ions derived from the associated species (apparently as a consequence of the conjugation between the heteroatoms), it does not alter the principal characteristics of the ionisation of nitrogen-containing organic compounds: mainly ions with saturated bonds are formed; they can be represented by ions with a quadrivalent positively-charged nitrogen atom having hybrid orbitals (Table 3). The efficiency of the ionisation of alkylhydrazines is higher; for example, the current density of the ions $(M - H)^+$ is approximately 10^{-2}–10^{-3} A Pa^{-1} cm^{-2} for trimethyl-, tetramethyl-, and dibutyl-hydrazines.

Comparison of data for the surface ionisation of a series of hydrazine derivatives[38], whose constituent atoms form the linkages >N–N=C< (hydrazones) –N=N– (azo-compounds) and >N–N=N–N< (tetrazenes), with data for the surface ionisation of alkylamines and alkylhydrazines shows that the ionisation efficiency of the radicals (M - H) decreases in the sequence amine > hydrazine > hydrazone > azo-compound [in the SI mass spectrum of tetramethyltetrazene the lines due to the ions $(M - H)^+$ are totally absent]; on the other hand, the ionisation efficiency of the molecules increases in this sequence (the mass spectrum of the primary ions of tetramethyltetrazene consists only of the lines due to the ions M^+). In contrast to hydrazines, the lines of $(M - Alk)^+$, caused by the ionisation of the species obtained on dissociation of the molecules at the N–C bond, are absent from the mass spectra of hydrazine derivatives. These differences can be accounted for by the decreased yield of reactions on the surface of the emitter which yield the above radicals rather than by the decrease in the ionisation potentials V_M of the molecules in the given series of compounds and the increase in the ionisation potentials of the radicals (M - H) and (M - Alk).

Table 3. The parameters of the SI mass spectra of certain alkylhydrazines[36].

Compound	*M*, a.u.	V_M, V	m_i, a.u.	Ion	Relative intensity, %	j, A cm^{-2}	T, K	V_i, V
1,1-Dimethyl-hydrazine	60	7.46 [45]	60	M^+	30	—		$7.35 \leqslant V \leqslant 7.8$
			59	$(M-H)^+$	100	$2\cdot10^{-10}$	1170	$\leqslant 7.4$
			45	$(M-CH_3)^+$	0.1	—		—
1-Ethyl-1-methyl hydrazine	74	—	74	M^+	60	—		$7.2 \leqslant V \leqslant 7.5$
			73	$(M-H)^+$	100	$5\cdot10^{-9}$	1200	$\leqslant 7.3$
			59	$(M-CH_3)^+$	8	—	»	—
			45	$(M-C_2H_5)^+$	0.7	—	»	—
Tetramethyl hydrazine	88	7.76 [46]	88	M^+	50	—		$\leqslant 7.2$
			87	$(M-H)^+$	100	$3.5\cdot10^{-8}$	1200	$\leqslant 7.15$
			85	$(M-3H)^+$	0.7	—	»	—
			73	$(M-CH_3)^+$	24	—	»	—
1,1-Di-n-butyl-hydrazine	144	7.57 [45]	144	M^+	6	—		$\leqslant 7.5$
			143	$(M-H)^+$	100	$2\cdot10^{-8}$	1150	$\leqslant 7.2$
			141	$(M-3H)$	15	—	»	—
			139	$(M-5H)$	5	—	»	—
			137	$(M-7H)$	0.7	—	»	—
			101	$(M-C_3H_7)$	100	$2\cdot10^{-8}$	1150	—
			99	$(M-C_3H_7-2H)$	15	—	»	—
			97	$(M-C_3H_7-4H)$	5	—	»	—
			87	$(M-C_4H_9)$	7	—	»	—
			85	$(M-C_4H_9-2H)$	2	—	»	—

The presence of a double bond in the molecules and the possible conjugation between the π-electrons and the electrons of the unshared pairs of the nitrogen atoms can result in the formation of a bond between the molecule and the emitter surface not only via the unshared pair of the nitrogen atom, as in the case of amines, but via the entire conjugated system of the electrons in the unshared pairs of the nitrogen atoms and the π -electrons. The adsorption of these molecules does not therefore entail a weakening of the β-bonds, as in the case of amines, and the yield of reactions with formation of the species (M - H) and (M - Alk) is correspondingly lower than in the adsorption of amines and their threshold ionisation temperatures are higher.

We may note that, although the surface ionisation efficiencies of hydrazine derivatives are smaller than those of the amines and hydrazines, they are nevertheless fairly high. Thus ionic current densities of approximately 10^{-4} A Pa^{-1} cm^{-2} can be obtained as a result of the surface ionisation of these substances.

The following differences between the characteristics of the surface ionisation of a series of *alkyl derivatives of phosphorus and arsenic* relative to amines have been discovered[47]:

1. The ionisation efficiencies of phosphines and arsines are much lower than those of amines and decrease in the series of compounds with heteroatoms in the sequence N > P > As. Thus, whereas in the ionisation of triethylamine the current density of the ions $(M - H)^+$ is $\sim 3 \times 10^{-2}$ A cm^{-2} Pa^{-1}, for triethylphosphine $j \cong 3 \times 10^{-4}$ A cm^{-2} Pa^{-1} and for tripropylarsine it is only 7×10^{-8} A cm^{-2} Pa^{-1}.

2. The decomposition of adsorbed molecules with formation of the radicals (M – R), which is characteristic of amines, does not occur in the case of phosphines and arsines: the intensity of the lines of the ions $(M - R)^+$ in the mass spectra of phosphines is low, while in the mass spectra of arsines the lines are altogether absent.

3. In the ionisation of phosphines and arsines the current of the ions M^+ is close in magnitude to that of the ions $(M - H)^+$, which indicates either a small difference between the ionisation potentials of the molecules and the radicals or a low yield of the reaction involving the formation of radicals in the adsorbed layer.

The characteristics of the surface ionisation of phosphines and arsines, relative to that of amines, enumerated above are associated with the difference between the electronic structures of the heteroatoms in these molecules. The orbitals of the unshared electron pair of the P and As atoms have a more pronounced *s* character than in the nitrogen atom, which should lead to a decrease of the probability of the formation of ions with an sp^2-hybrid structure. Furthermore, the P and As atoms have unoccupied *d* orbitals with relatively low energies, as a result of which they are capable of accepting electrons. Therefore in the adsorption of phosphines and arsines the withdrawal of the unshared pair of the heteroatom to the emitter can be accompanied by the capture of electrons from the emitter in the unoccupied *d* orbital. The latter should weaken the negative inductive effect of the adsorbed molecules and decrease the probability of their dissociation at the β-bonds.

V. THE FORMATION OF VIBRATIONALLY-EXCITED IONS IN THE SURFACE IONISATION OF ORGANIC COMPOUNDS AND THE CHARACTERISTIC FEATURES OF THEIR UNIMOLECULAR DECOMPOSITION REACTIONS

The mass spectra of almost all compounds contain, together with the narrow lines due to the primary ions which have been desorbed from the surface of the emitter and which have "reached" the collector of the mass-spectrometer, also broadened lines due to fragment ions—the products of unimolecular decomposition reactions of primary ions during their movement within the space of the mass-spectrometer.

A pair of lines due to fragment ions in the SI spectrum corresponds to each decomposition of the primary ions $m^+ \rightarrow m_1^+ + m_2$ (Fig.4): the decomposition of ions in the acceleration region within the ion source leads to the appearance of lines corresponding to the mass of fragment ions m_1, which have broadened in the direction of low masses or low energies of the ion; the same decomposition within the field-free region of the mass-spectrometer, between the accelerating electrodes of the source and the magnetic field zone, leads to the appearance in the mass spectrum of broadened lines due to ions with an apparent mass $m^* = m_1^2/m$.[48] The decomposition process can be unambiguously identified on the basis of the pair of lines recorded. By virtue of the high intensity of the lines due to the primary ions and the small number of lines in the SI mass spectra, it is therefore possible to identify the lines of the fragment ions whose intensity is many times smaller (by a factor of up to approximately 10^6) than the intensity of the lines due to the primary ions.

The ions obtained by surface ionisation obey the Boltzmann energy distribution as a function of the emitter temperature *T*; the energy is determined by *T* and the number of vibrational degrees of freedom of the ionising species [in the classical approximation the total vibrational energy stored in the species on the surface of the emitter before evaporation is $(3N-5)kT$, where *N* is the number of atoms in the species]. Some of the ions, whose total vibrational energy exceeds the energy of a decomposition reaction, can dissociate in the course of their travel through the mass-spectrometer.

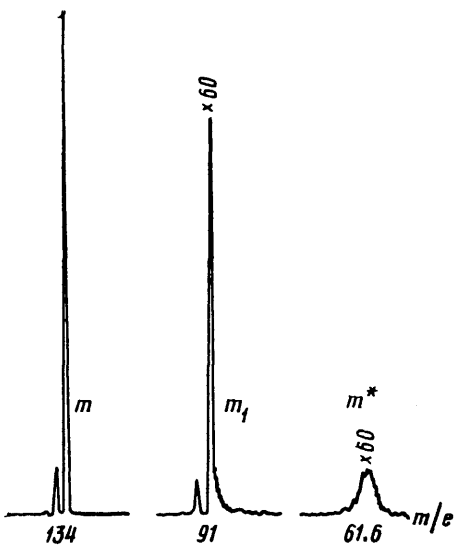


Figure 4. The lines due to the primary and fragment ions in the SI mass spectrum of benzyldimethylamine.

The unimolecular decompositions of the ions formed via surface ionisation are slow processes; the lifetimes of the ions are such that before decomposition they are able to execute more than 10^6–10^7 internal vibrations[34], which suggests that the decomposition reactions of the ions after their desorption from the surface of the emitter take place as a result of a statistical redistribution of the excitation energy within the ion; the energy being concentrated in such a way that a specific configuration of the activated complex, leading to its dissociation, is attained; the statistical theory of mass spectra can be applied to the description of such decomposition reactions[49].

The temperature variations of the ratios of the currents of fragment ions to the current of the parent ions make it possible to find the activation energies ε* for decomposition reactions which occur after the ions have moved for a specific time[24] (Fig.5). The true activation energy for the decomposition reactions or, in the case of direct decompositions, the bond dissociation energy in the ion can be determined from the values of ε* with the aid of the statistical theory of mass spectra[50,51].

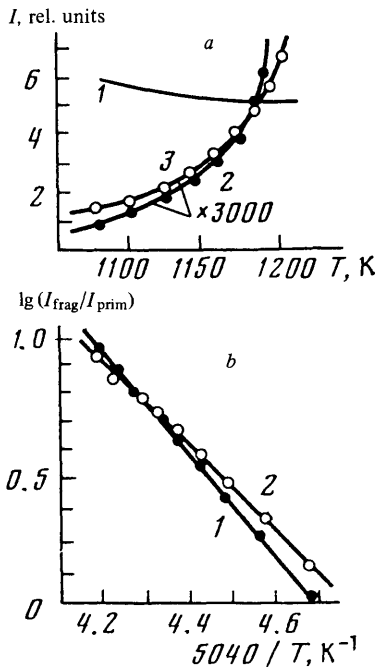


Figure 5. *a*) Temperature variation of the currents in the ionisation of diethylamine [*1*) for primary $(M - H)^+$ ions; *2*) for fragment ions with $m_1 = 44$ a.u.; *3*) for fragment ions with $m^* = 26.9$ a.u.; *b*) Arrhenius plots for the ratios of the fragment ion currents [*1*) m_1; *2*) m^*] to the primary ion current[32].

All the known types of unimolecular decomposition reactions of ions can be traced in the SI mass spectra: direct decompositions, decompositions with rearrangement, and multistage decompositions. In most cases the decomposition reactions of the ions obtained by surface ionisation belong to the type with rearrangements and to the multistage type and lead to the formation of stable fragments, which as a rule do not have unpaired electrons (Fig.6).

The mechanisms of the fragmentation of ions of different classes of organic compounds which have been deduced and the discovery of the characteristics of their decomposition pathways[33,36,38,47] are important for the purposes of the surface ionisation mass-spectrometry of organic compounds, since the primary ion can be "assembled" from the fragment ions (Fig.6).

Comparison of the decomposition reactions of ions obtained by surface ionisation (reliably identified experimentally), for which theoretical calculations have been made, with the decomposition reactions of the excited ions formed in collisions with electrons (with the mass spectrum generated as a result of ionisation by the electrons) can serve as a definite criterion of the applicability of the quasi-equilibrium theory to the description of the electron ionisation mass spectra[36,52] and in many instances can help in the determination of the pathways leading to the decomposition reactions on ionisation by electrons[38,52].

VI. SURFACE-IONISATION MASS-SPECTROMETRY OF ORGANIC COMPOUNDS

The set of results described constitutes the physicochemical basis of the method of the surface-ionisation mass-spectrometry (SIMS) of organic compounds. At the present

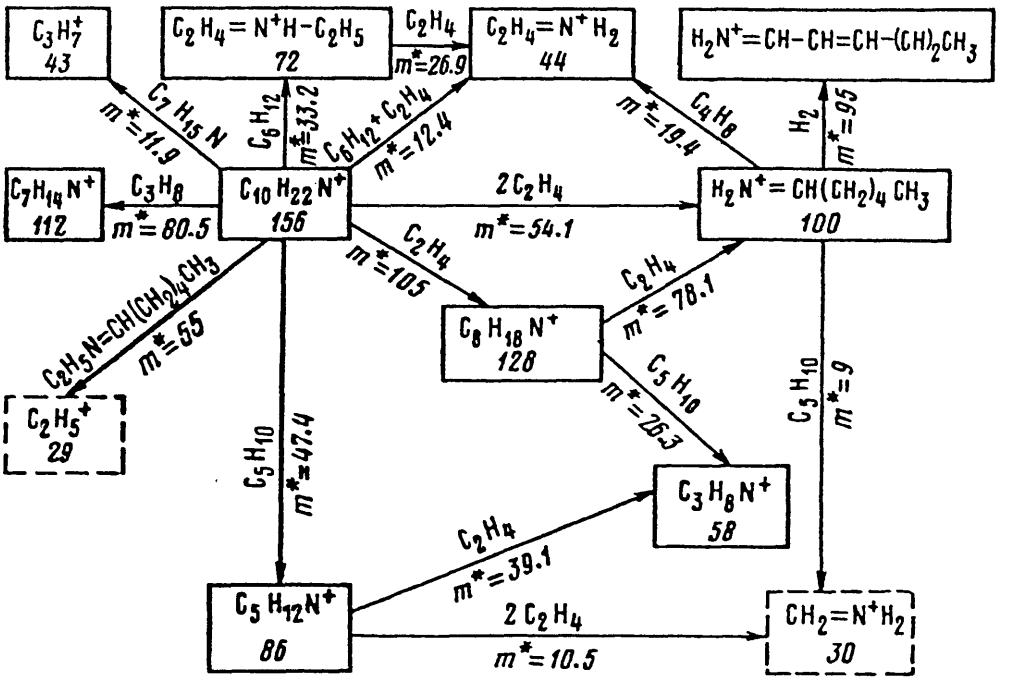


Figure 6. Unimolecular decompositions of the diethylhexylamine ions $(M - H)^+$.[33]

time SIMS can be applied only to specific classes of organic compounds with Group VA heteroatoms. However, the abundance and importance of these compounds are considerable. Certain fields of application of SIMS are examined below.

1. Application in Physicochemical Research

The following applications of SIMS are possible at the present time:

1. For the generation of fluxes of ions derived from organic compounds with considerable ion densities (up to 10^{-1}–10^{-2} A Pa^{-1} cm^{-2}). Their characteristic feature is a small scatter of the initial energies as a consequence of the Maxwell velocity distribution of ions as a function of the temperature of the emitter. The energy of the vibrational excitation of the ions can be readily regulated by altering the temperature of the emitter, which can be used in many problems, for example in the study of the influence of the vibrational excitation of ions on the kinetics of ion–molecule reactions.

2. For the detection of heterogeneous reactions from the chemical composition of the ions. The γ_i–T relations can be found by Eqns.(7)–(9) from the I_i–T relations for known $\beta_i(T)$ functions together with the concentration relations as a function of T for the ith species on the surface proportional to $\gamma_i(T)$. It is also possible to discover certain reactions with rearrangement on the surface, as can be seen from the ionisation of the molecules of ethyl-n-pentylamine, which have been partly converted into the molecules of *N*-ethylpiperidine[53].

3. For the estimation of the lifetimes of the vibrationally-excited ions with respect to unimolecular decomposition[34] and also for the determination of the activation energies ε for such decomposition reactions involving ions[24,50,51]. So far as we are aware, there are at present no other experimental methods for the determination of ε for reactions involving ions which would not require the knowledge of the thermochemical constants of the ions.

4. For the determination of the kinetic characteristics of the thermal desorption of species. We shall consider this problem in greater detail since it was not considered previously.

The kinetic characteristics of thermal desorption, namely the average lifetimes $\tau(T)$ of the adsorbed species relative to the desorption of ions and neutral species, the activation energies E^+ and E^0 for the desorption of these species, and the pre-exponential factors C and D in the equation for the flux of desorbed species $\nu^+ + \nu^0 = N[C \exp(-E^+/kT) + D \exp(-E^0/kT)] = N/\tau$ (N is the concentration of species on the surface) are the most important characteristics of the interaction of the species with the solid. The non-stationary processes ($\nu^+ + \nu^0 \neq \nu$), in which N varies with time, are used for their determination. The measured ionic currents are proportional to N.

The study of the ionisation of polyatomic organic molecules and radicals under non-stationary conditions is complicated by the simultaneous presence on the surface of the emitter of species of different composition, involved in reactions via many channels, which causes an additional variation of N_i as a function of time.

The present authors and their coworkers[23,54,55] analysed the possibility of determining the kinetic characteristics of the desorption of polyatomic species taking into account the reactions in the surface layer and using two isothermal methods for creating non-stationary conditions, which are explained in Fig.7: by modulating the potential at the surface of the emitter[56] (for $\beta_i > 0.1$) and by modulating the density of the incident molecular flux[57]. The solutions of the differential equations describing the time variation of N_i in each method made it possible to elucidate the significance of the measured characteristics, including those for the ionisation of molecules on inhomogeneous surfaces. As a rule τ is determined by the decrease of the number of species on the surface as a consequence of the processes occurring on the latter and is thus a quantity of practical importance. In many special cases it is possible to isolate $\tau_i^+(T)$ and $\tau_i^0(T)$ and correspondingly E_i^+ and E_i^0. In the case of non-uniform surfaces, all the parameters determined are effective; their magnitude approaches that of the characteristics of the desorption from the sections of their surface with the highest values of ϕ.

The quantities $\beta_i' = \beta_i/\{1 + [k_d/(k_0 + k_+)]_i\}$, where k_d, k_0, and k_+ are the rate constants for the dissociation and thermal desorption of the neutral ith species and the thermal desorption of their ions respectively, which are similar to the ionisation coefficients β_i, can be found from Fig.7 under conditions corresponding to the modulation of the potential with respect to the currents I_{i2} and I_{i1}. Evidently $\beta_i' < \beta_i$ and it is therefore possible to estimate the upper limit of the possible values of V_i from the β_i' with the aid of Eqns.(3) and (5). These estimates of V_i are more accurate than those based on the stationary currents defined by Eqns.(6) and (7) and do not require the knowledge of many quantities entering into these formulae which are difficult to determine.

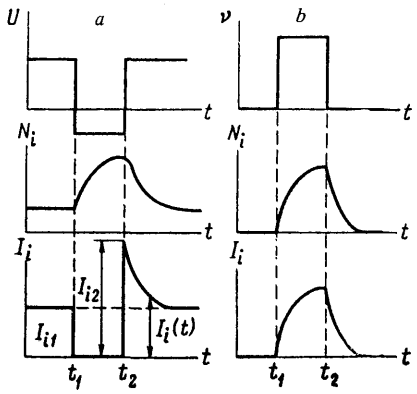


Figure 7. Illustration of the potential modulation method (*a*) (the rectangular waveform of the ion-arresting potential is switched on for the period from t_1 to t_2; ν = const.; T = const.) and of the flux density modulation method (*b*) (the molecular flux is introduced during the period from t_1 to t_2; U = const.; T = const.).

Table 4 presents the effective kinetic characteristics of the desorption and the values of β' obtained by the potential modulation method for several radicals formed from triethylamine, tributylamine, and tetramethyldiaminomethane when they are ionised on oxidised tungsten wires. These were the first determinations by the SI methods for species of such complex composition. Evidently the activation energy for the desorption of the ions is small. Because of this, the threshold temperatures for the ionisation of the radicals on oxidised tungsten wires are low; they are lower than for the ionisation of the corresponding fluxes of Cs atoms.

The quantities τ in the experimental temperature (T) ranges amount to tens–hundreds of milliseconds; such times are sufficient for the attainment of full thermal equilibrium in the adsorbed layer of species.

5. For the determinations or estimates of the ionisation potentials of species forming positive ions. The potentials V of species undergoing surface ionisation can be determined in different ways: (1) from the slopes of the plots of $\lg I_i = f(1/t)$ when the $I_i - T$ relation is exponential [Eqn.(8)] and the $\gamma_i - T$ relation may be disregarded[36,42]. It is then assumed that the ratio of the partition functions A_i is virtually independent of T. The error associated with this assumption is of the order of magnitude of $\sim kT$, which has been confirmed by the determinations of V for the molecules of aniline[42] and other compounds whose ionisation potentials had been determined by other methods[30]: (2) from the maximum current density and the corresponding temperature T. The value of β_i is found by Eqn.(6) and from it V_i is determined using Eqns.(3) and (5); it is then assumed that $\gamma_i(T) = 1$ and ν is found from the vapour pressure of the test substance in the apparatus. If the pressure is measured with an ionisation gauge calibrated with respect to nitrogen, then the experimental values of β are smaller than the true values and the ionisation potentials are correspondingly larger than the true values. Since the ionisation potentials V of radicals with Group VA heteroatoms are as a rule unknown[18], even estimates of their possible limiting values are of interest. The majority of the estimates have been made by this method. (3) From the values of β' obtained by the potential modulation method which is feasible for $\beta' \geq 0.1$.

Table 4. Kinetic characteristics of the thermal desorption of certain nitrogen-containing radicals from oxidised tungsten wires non-uniform with respect to emission.

Radical	E_+^* ±0,1, eV	lg C^*	β' (T)	E_0^* ±0,1, eV	lg D^*	Refs.
$C_2H_5NC_2H_4C_2H_5$	1.7	12.0±0.4	0.9 (900 K)	—	—	[23]
$C_2H_5NC_2H_5CH_2$	1.2	9.4±0.4	1.0 (840 K)	—	—	[23]
$(C_4H_9)NC_4H_8C_4H_9$	1.7	12.5±0.4	0.9 (900 K)	—	—	[23]
$(CH_3)_2NCHN(CH_3)_2$	1.0	8.3±1.0	0.99 (840 K)	2.1±0.1	12±1	[54]
$(CH_3)_2NCH_2$	1.5	11.0±1.0	0.88 (800 K)	1.5±0.1	10±1	[54]

Table 5 presents the values of V determined or estimated by the surface ionisation method. Evidently many radicals derived from nitrogen-containing compounds have relatively low ionisation potentials.

2. Applications in the Analytical and Structural Chemistry of Organic Compounds

The characteristic nature of the SI mass spectra of organic compounds and the simple rules governing the formation of ions and permitting the prediction of their composition in the mass spectra and the estimation of the current densities corresponding to the lines indicate the possibility of employing the SIMS in the analytical and structural chemistry of organic compounds. We shall examine certain possibilities of the analytical method based on the use of SIMS.[30,59]

The molecular weight of the substance analysed can be determined from the lines of the ions $(M - H)^+$ and, more rarely, from those of the ions M^+ and $(M + H)^+$. In all cases the characteristic form of the $I-T$ relations for each of these types of ions helps in their identification (Fig.2): the current of the ions M^+ as a rule increases with increasing temperature[30,36,47]. The mass numbers of the radicals R^i can be found from the $(M - R^i)^+$ lines; the current densities of the ions $(M - H)^+$ and $(M - R^i)^+$ yield information about the electronegativities of the substituents R^i; the $(M - H - 2nH)^+$ and $(M - R^i - 2nH)^+$ lines make it possible to assess the degree of saturation of the hydrocarbon substituents R^i. Finally, information about the structure of each primary ion can be obtained from the lines of its fragment ions (Fig.6).

Table 5. Ionisation potentials of certain molecules and radicals with Group VA heteroatoms.

Compound	Ionising species	V, V	Refs.
Ethylamine	(M+H)	$\lesssim$7.8	[32]
"	(M—H)	$\lesssim$8.3	[32]
Pentylamine	(M+H)	$\lesssim$7.7	[31]
"	(M—H)	$\lesssim$8.0	[31]
Aniline	M	7.65±0.07	[42]
Dimethylamine	(M+H)	$\lesssim$7.7	[30]
"	(M—H)	$\lesssim$8.3	[30]
Diethylamine	(M+H)	$\lesssim$7.2	[32]
"	(M—H)	$\lesssim$7.2	[58]
"	(M—3H)	$\lesssim$7.4	[32]
"	(M—CH_3)	$\lesssim$7.8	[32]
Piperidine	(M+H)	$\lesssim$7.6	[31]
"	(M—H)	$\lesssim$7.2	[31]
Pyridine	(M+H)	$\lesssim$7.5	[31]
Trimethylamine	(M—H)	$\lesssim$7.1	[30]
Triethylamine	(M—H)	$\lesssim$6.9	[32]
"	(M—3H)	$\lesssim$7.2	[32]
"	(M—CH_3)	$\lesssim$7.1	[32]
Dimethyloctylamine	(M—H)	$\lesssim$6.9	[30]
"	(M—C_7H_{15})	$\lesssim$7.1	[30]
Diethylhexylamine	(M—H)	$\lesssim$6.9	[30]
"	(M—CH_3)	$\lesssim$7.0	[30]
"	(M—C_5H_{11})	$\lesssim$7.0	[30]
Butyldipropylamine	(M—H)	$\lesssim$6.9	[30]
"	(M—C_2H_5)	$\lesssim$7.0	[30]
"	(M—C_3H_7)	$\lesssim$7.0	[30]
Ethyldimethylamine	(M—H)	$\lesssim$7.1	[34]
"	(M—CH_3)	$\lesssim$6.3	[54]
Allyldimethylamine	(M—H)	$\lesssim$7.1	[34]
"	[M—(CH=CH_2)]	$\lesssim$6.3	[54]
Tetramethyldiaminoethane	M	$\lesssim$7.8	[34]
"	(M—H)	$\lesssim$6.1	[54]
"	[M(CH_3)$_2$]	$\lesssim$6.3	[54]
"	(CH_3)$_2$N	$\lesssim$7.7	[34]
Cyano-*N*,*N*-dimethylaminomethane	(M—H)	$\lesssim$8.1	[30]
"	(M—CN)	$\lesssim$6.3	[34]
Benzyldimethylamine	(M—H)	$\lesssim$7.0	[34]
"	(M—C_6H_5)	$\lesssim$6.3	[54]
Dimethyl-*p*-nitrobenzylamine	(M—H)	$\lesssim$8.0	[34]
"	(M—$C_6H_5NO_2$)	$\lesssim$6.3	[54]
6-(9′-Acridinyl)-1-ethyl-1,2,3,4-tetrahydroquinoline	M	$\lesssim$7.2	[37]
2-Phenylbenzimidazole	M	7.0÷7.3	[37]
Methylhydrazine	M	7.53±0.08	[36]
"	(M—H)	$\lesssim$7.4	[36]
1,1-Dimethylhydrazine	M	7.35$\lesssim V \lesssim$7.8	[36]
"	(M—H)	$\lesssim$7.4	[36]
Trimethylhydrazine	M	7.2$\lesssim V \lesssim$7.5	[36]
"	(M—H)	$\lesssim$7.3	[36]
Tetramethylhydrazine	M	$\lesssim$7.2	[36]
"	(M—H)	$\lesssim$7.15	[36]
"	(M—CH_3)	$\lesssim$7.3	[36]
1-Ethyl-1-methylhydrazine	M	7.3$\lesssim V \lesssim$7.5	[36]
"	(M—H)	$\lesssim$7.3	[36]
1,1-Di-n-butylhydrazine	M	$\lesssim$7.5	[36]
"	(M—H)	$\lesssim$7.2	[36]
"	(M—C_3H_7)	$\lesssim$7.2	[36]
Acetone n-propylhydrazone	(M—H)	$\lesssim$7.1	[38]
Acetone isopropylhydrazone	(M—H)	$\lesssim$7.1	[38]
Azopropane	M	$\lesssim$7.2	[38]
"	(M—H)	$\lesssim$7.2	[38]
Tetramethyltetrazene	M	$\lesssim$7.1	[38]
Diethylphosphine	(M+H)	$\lesssim$7.8	[47]
"	(M—H)	$\lesssim$8.2	[47]
Triethylphosphine	(M+H)	$\lesssim$7.4	[47]
"	M	$\lesssim$7.8	[47]
"	(M—H)	$\lesssim$7.4	[47]
Tripropylphosphine	(M+H)	$\lesssim$7.8	[47]
"	M	7.8$\lesssim V \lesssim$8.2	[30]
"	(M—H)	$\lesssim$8.2	[47]
"	M	$\lesssim$8.3	[47]
"	(M—H)	$\lesssim$8.0	[47]

The small number of lines in the mass spectra facilitates the analysis of mixtures of substances. The degree of coverage of the emitter by the molecules of the test substances at temperatures above the threshold value for ionisation is low and the molecules in the adsorbed layer do not interact. Therefore the mass spectra of mixtures of different amines, hydrazines, and their derivatives are the sum of the mass spectra of the individual components[30,32]. The characteristic form of the $I-T$ relations for ions of each type makes it possible to distinguish, for example, the ions $(M_1 - H)^+$ from the ions $(M_2 - R)^+$ having identical masses. The high selectivity of surface ionisation can be used to determine minute trace amounts of amine impurities in mixtures of substances which are non-ionisable or weakly ionisable by surface ionisation. For example, tertiary alkylamines and their derivatives, present in amounts of $\geq 10^{-7}-10^{-8}$%, can be analysed with the aid of SIMS.[30]

The high efficiency of the surface ionisation of amines, hydrazines, and derivatives of substances of these classes is responsible for the high sensitivity of the analysis by the SIMS method, which significantly exceeds the sensitivity of the analysis using electron impact mass spectrometry. Thus, in the surface ionisation of tertiary amines and their derivatives, it is possible to obtain from an oxidised tungsten emitter having an area of 1 cm^2 currents of approximately 10^{-1} A Pa^{-1}, whereas currents of approximately $10^{-4}-10^{-6}$ A Pa^{-1} are obtained in the ion sources of mass spectrometers with electron ionisation. In this connection SIMS is promising for the analysis of bio-organic substances whose isolation even in microamounts requires as a rule the processing of a large amount of the initial material of biogenic origin. The study of the surface ionisation of the alkaloid allomatrine, vitamin B_2, riboflavin, and the acetylcholine mediator makes analysis simpler when SIMS is employed and its sensitivity is significantly higher than for mass spectrometry with ionisation by electrons[30,37]. The likelihood of SIMS being useful for the determination of the aminoacid sequence in peptides has been examined[30] and it has been concluded that, at least for relatively short peptides, the application of surface ionisation makes it possible to simplify the mass-spectrometric analysis and to increase significantly its sensitivity compared with the mass spectrometric analysis involving ionisation by electrons.

An important property of the ions obtained by surface ionisation, which distinguishes them from the ions formed using other ionisation procedures, is their definite energy characteristic: with equipartition of energy among the internal degrees of freedom, the ions have a Boltzmann distribution (as a function of the emitter temperature) with respect to the total internal energy. We believe that this property makes it useful to employ SIMS in the solution of one of the important problems of organic mass spectrometry—the determination of a relation between the reactivity of a compound and its mass spectrum.

The state of the knowledge of the characteristic features of surface ionisation of organic compounds and the possibility of employing the surface ionisation phenomenon for analytical and other purposes is at present sufficient to develop practical surface-ionisation mass spectrometry. The design of the surface-ionisation ion sources is simple; much experience has been gained in their development for mass spectrometers designed for isotope analysis. After a minor redesign of commercial mass-spectrometers (for example, by providing the mass spectrometer for isotope analysis with a system for the injection of the vapours of organic substances or by fitting the mass spectrometers for the analysis of organic compounds with a surface-ionisation ion source), they can be used also for the surface-ionisation analysis of organic compounds. The SI mass spectra of a series of cyclic amines obtained using the MI-1201 mass spectrometer[60,61]# can serve as an example of this.

VII. SURFACE-IONISATION DIODE DETECTORS OF ORGANIC COMPOUNDS

The high efficiency of the surface ionisation of amines, hydrazines, and their derivatives can be used for the sensitive and selective detection of microamounts of the above substances, for example, in air or in mixtures in the course of their chromatographic separation. It is then evident that detection can be achieved not only mass-spectrometrically but also with the aid of simple diode devices in which the overall ionic current between the emitter and the collector is measured[62,63].

The possibility of the practical realisation of surface ionisation in a diode device under the conditions of its separation not only *in vacuo* but also in air or in other gases has now been elucidated: ways have been found for the preparation of effective emitters operating in different media[27,64]; the designs of flow-type devices ensuring the virtually complete deposition of the substances analysed on the surface of the emitter have been developed[65,66]; the optimum operating conditions for diode detectors have been established[65,67]. The first surface-ionisation devices and highly selective methods for the detection of organic compounds belonging to the classes of amines, hydrazines, and their derivatives, which are unique as regards sensitivity, have been developed[64-67]. For example, with the aid of a diode surface-ionisation detector of simple design, it is possible to measure the content in air of tertiary alkylamines and their derivatives in an amount down to approximately $10^{-14}-10^{-15}$ litre^{-1}.[65]

The surface-ionisation detectors are designed for the following purposes.

1. For the monitoring of the contamination by gases of industrial premises as part of safety techniques. The "Valdai" surface-ionisation gas-analyser was developed in 1976 for the continuous monitoring of the contamination of industrial premises with gaseous diethylamine[68]. After appropriate calibration, it can be used also for the determination in air of microamounts of other secondary and tertiary alkylamines and their derivatives.

2. For the highly sensitive detection of leaks in hermetically-sealed compartments (containers, tubes, etc.). We may note that, when halogen leak-seeking devices are replaced by the more sensitive amine devices, the contamination of the upper atmosphere by Freon is prevented.

3. For gas chromatography. The surface-ionisation detector (SID) for gas chromatography has the following characteristics[65]: ionisation efficiency $\sim 4 \times 10^{-2}$ (with respect to triethylamine), background current $\sim 10^{-11}$ A, noise level $\sim(2-10) \times 10^{-14}$ A, threshold sensitivity $\sim 5 \times 10^{-15}$ g s^{-1} (with respect to triethylamine), linear range $\sim 10^4-10^8$, errors of readings $\leq \pm 5$% (with respect to triethylamine), continuous operation time ≥ 50 h, and selectivity with respect to hydrocarbons $\sim 10^5-10^8$.

#Unfortunately in the above investigations the authors, who obtained the mass spectra at an emitter temperature of approximately 2000 K, do not draw a distinction between the primary and fragment ions, which reduces the amount of information available from the SI mass spectra.

It is important that, in contrast to virtually all the existing selective detectors, the SID is selective with respect to the nature of the functional group containing the nitrogen atom and not with respect to the heteroatom itself[62]. It can therefore be used for the functional gas-chromatographic (GC) analysis of nitrogen-containing compounds[69]. Thus, using the simultaneous detection of the components at the outlet from the gas-chromatographic column by the SID and the flame-ionisation detector (FID), it is possible to determine the type of amino-group in aliphatic amines: when, for example, the Pye-Unicam FID is used, the SID/FID signal ratio is $\sim 10^3$–10^4 for tertiary amines, $\sim 10^2$ for secondary amines, and ~10 for primary amines[69,70].

The high SI efficiency with respect to tertiary alkylamines, significantly exceeding the SI efficiency for all other classes of organic compounds, can be used for the equisensitive detection with the aid of the SID of any organic compounds in mixtures in the course of their gas-chromatographic separation: by passing a tertiary alkylamine at a constant concentration together with the carrier gas through the gas-chromatographic column and by recording with the aid of the SID the variation of its volume concentration during the passage of the mixture components through the detector, it is possible to determine the volume concentrations of the components[71].

4. For the solution of any special problems in which the detection and identification of submicroamounts of amines and their derivatives is required, for example, of traces of toxic substances for the protection of the environment, for the identification of amines which are the active principles of an odour, for the determination of trace amounts of alkylamines and their derivatives in hermetically-sealed volumes, for the analysis of amines evolved by living organisms, etc.

In conclusion we may note that, when an additional initial stage involving the chemical conversion of the substances analysed into amines is used in the surface ionisation detection method, the latter can become universal and suitable for all substances capable of such conversion. For example, *N*-nitroso-compounds can be readily converted into amines by denitrosation; therefore the SID can be used for the determination of the contents of carcinogenic *N*-nitroso-compounds in food products and in the environment.

* * *

Thus it has only been recently established that organic compounds are capable of forming stable polyatomic positive ions via surface ionisation. As a result of the investigation of the characteristic features of this phenomenon for compounds with Group VA heteroatoms, extensive possibilities have arisen for the employment of surface ionisation in the physical and analytical chemistry of these compounds. The uniquely high sensitivity of the detection with the aid of surface ionisation of microamounts of many substances in the atmosphere and in other mixtures is of great practical importance.

There are already indications that compounds of other classes can also be ionised by surface ionisation[19,30,72–75]. There is no doubt that the further search for compounds capable of surface ionisation and the study of the characteristic features of their ionisation will significantly extend the applications of the phenomenon.

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A New Class of Complex Water-soluble Polyelectrolytes

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The literature data on polyelectrolyte complexes (PEC), mainly non-stoichiometric PEC (N-PEC), are analysed. Interpolyelectrolyte reactions, leading to the formation of N-PEC as well as the methods of synthesis of these macromolecular compounds are examined. The structure of water-soluble N-PEC, which constitute a new class of complex water-soluble polymers, is discussed. A special section is devoted to the behaviour of N-PEC in aqueous salt media and to the description of the characteristics of the phase separation in such systems. The prospects for the development of the research into and the possible applications of this new class of polyelectrolytes are discussed.
The bibliography includes 64 references.

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I INTRODUCTION

The increasing interest in the chemistry and physical chemistry of synthetic polyelectrolytes is due to the continuous expansion of their practical applications as highly effective flocculants, structure-forming agents and stabilisers for colloidal dispersions, ion-exchange materials, specific sorbents, biologically active compounds, etc. In addition, with their aid it is sometimes possible to simulate certain important features of the behaviour of biopolymers: enzymes and nucleic acids.

Polyelectrolytes belong to the class of reactive polymers. Among the reactions which they undergo, one of the most interesting is that between cationogenic and anionogenic macromolecules (polymeric acids, polymeric bases, and their salts) in aqueous solutions, leading to the formation of interpolymer salts or polyelectrolyte complexes (PEC), a term which is frequently applied to them. In a certain sense, this reaction has no analogies in the chemistry of low-molecular-weight substances, since the polymeric product (the PEC) is a compound whose stability is due mainly to entropy factors. Cationo- and aniono-genic macromolecules complement each other electrostatically. Therefore the interaction between them is fully analogous in the thermodynamic sense to the interaction between complementary biopolymers responsible for the self-assembly of the majority of biological structures.

As early as the 1930's, the attention of investigators was attracted to the fact that, when aqueous solutions of oppositely charged natural polyelectrolytes, characterised by a relatively low charge density on the macromolecules (for example, gelatines and gum arabic), are mixed, phase separation and the formation of living coacervates take place under certain conditions[1-4]. Subsequently the phase separation conditions were investigated[5-7]. On the other hand, the chemical and physicochemical aspects of the reactions between the macromolecules and particularly the structure of the PEC have not been investigated at the macromolecular level. The coacervates of natural polyelectrolytes still attract the attention of certain biochemists attempting to simulate the phenomena of prebiological evolution[8-10].

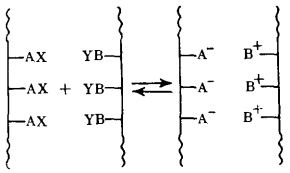
The next stage in the studies on the PEC refers to the 1960's [11-15] when strong polyelectrolytes with a high charge density on the chains became available as a consequence of advances in the synthesis of polymers. The interaction in solutions between electrostatically complementary polyelectrolytes, characterised by a high charge density, leads to the formation of PEC, which are usually precipitated from solution in the form of comparatively little solvated deposits. The ratio of the oppositely charged groups in these compounds is 1 : 1. Henceforth we shall refer to such PEC as stoichiometric (S-PEC). They are insoluble in any of the known solvents and are capable of limited swelling in water, resembling in some of their properties the well-known cross-linked hydrogels. The interest in the S-PEC is due mainly to the possibility of using them as membranes for the desalination of water[14-15], for haemodialysis[16-18], etc. A fairly large number of publications have been devoted to the formation reactions and properties of S-PEC (see, for example, Refs.19–27), a detailed description of which is outside the framework of our task.

The present review deals with a new field of research which has arisen as a result of the discovery of non-stoichiometric PEC (N-PEC). These interpolymer compounds are also the products of reactions between electrostatically complementary chains. However, in contrast to the S-PEC, when certain conditions are observed, they do not precipitate. Consequently they can be used like the usual soluble polyelectrolytes. At the same time, in contrast to the usual polyelectrolytes, the N-PEC also have a series of unique properties, which, as will be seen from the exposition below, make it possible to isolate them as a special class of water-soluble polymeric compounds.

However, before proceeding to the description of the N-PEC, it is necessary to consider certain general characteristics of interpolyelectrolyte reactions and their products.

II. INTERPOLYELECTROLYTE REACTIONS

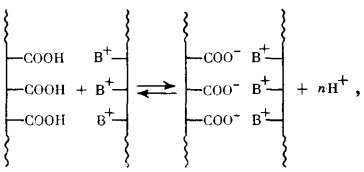
The reaction between polyelectrolytes can be represented schematically as follows:



(I)

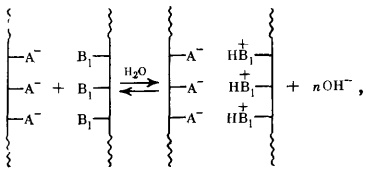
Here -AX- is a unit of a polymeric acid or its salt and -BY- is a unit of the polymeric base or its salt. As a result of the reaction between the units of the macromolecule, salt bonds are produced. The formation of each bond is accompanied by the liberation into the surrounding medium of a pair of low-molecular-weight ions.

Evidently equilibrium (I) can be displaced in one direction or another by altering the activity of the low-molecular-weight reaction product. Accordingly, one of the methods for the investigation of equilibrium (I) is based on the measurement of the activities of the low-molecular-weight ions in the system. This can be done particularly simply when the reaction is accompanied by the liberation of protons or hydroxide ions, which happens when one of the macromolecular reactants is a weak polymeric acid or a weak polymeric base, and the second is a polymeric cation or a polymeric anion respectively:



(Ia)

where B^+ is, for example, a charged amino-group and



(Ib)

where A^- is an anionic group in the unit of the polymer chain and B_1 is, for example, a primary, secondary, or tertiary amino-group. Reactions of types (Ia) and (Ib) can then be investigated by the potentiometric titration method[19-23].

The typical pH profiles of such reactions are illustrated in Fig. 1 The degree of conversion θ represents the fraction of the intermacromolecular salt bonds formed relative to their maximum possible number. An equilibrium value of θ corresponds to each pH. The value of θ can be readily calculated from potentiometric titration data. It is determined as the ratio of the concentrations of the salt bonds (c_S) and the initial concentration of the functional groups of any of the polyelectrolytes (c_0)† provided that the PEC species remain stoichiometric over the entire range of θ.

†Here and henceforth the concentration of the polyelectrolytes will be expressed in terms of the molar concentration of their units and will be designated as follows: basic mol litre^{-1}.

Since the formation of each intermacromolecular salt bond is accompanied by the liberation of a proton [reaction (Ia)] or a hydroxide ion [reaction (Ib)] into the surrounding medium, the following equation can be used to determine c_S and hence also θ:

$$c_c = \theta c_0 = q_{alk}/V + [H^+], \quad (1a)$$

where q_{alk} is the amount of the added titrant (alkali), $[H^+]$ the concentration of protons in solution, V the volume of the reaction mixture, and

$$c_c = \theta c_0 = q_{ac}/V + [OH^-], \quad (1b)$$

where q_{ac} is the amount of added titrant (acid) and $[OH^-]$ the concentration of hydroxide ions in solution. Reactions whose θ–pH profiles have a positive slope correspond to equilibrium (Ia) and those with a negative slope correspond to equilibrium (Ib).

Fig. 1 shows that the profiles of reactions (Ia) and (Ib) are very steep, which is usually characteristic of cooperative transformations. The transformation of a mixture of macromolecules which have not interacted ($\theta = 0$) into the product of the completed reaction ($\theta = 1$) takes place over a fairly narrow pH range. Correspondingly the pH range in which the PEC formed is stable proves to be fairly wide.

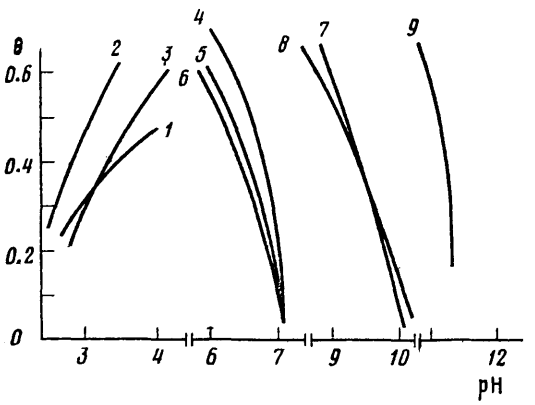
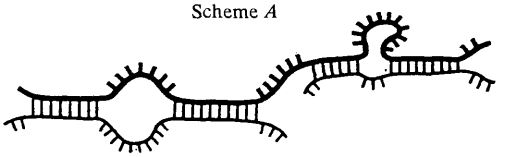


Figure 1. Dependence of the degree of conversion θ on the pH for reactions between polyelectrolytes: *1*) polyacrylic acid (PAA)–poly(dimethylaminoethyl methacrylate) hydrochloride (PDMAEMA.HCl); *2*) poly-L-glutamic acid–PDMAEMA.HCl; *3*) PAA–poly-L-lysine hydrobromide (PL.HBr); *4*) poly-4-vinylpyridine (PVP)–sodium polyphosphate (PP-Na); *5*) PVP–sodium polyethylenesulphonate; *6*) PVP–sodium polystyrenesulphonate; *7*) PDMAEMA–sodium polyacrylate (PA-Na); *8*) PDMAEMA–PP-Na; *9*) PL–PA-Na.[20]

The results of the study of the equilibria of the reactions involving the formation of PEC have led to the idea that the PEC are polymers with a ladder structure in which more or less long sequences of pairs of units, linked via salt bonds, alternate with loops consisting of sequences of disconnected units[22,26,27] (Scheme *A*). The fraction of units incorporated in the ladder sequences increases with θ. The average length of the ladder sequences also increases,

as shown by the results of the analysis of equilibria (Ia) and (Ib) in terms of model *A*:[27]

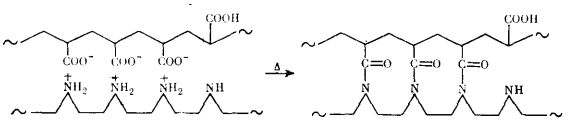
Scheme *A*



The study of the properties of S-PEC, which are products of completed reactions, indicates the presence in the latter of a considerable number of defects, which are represented in Scheme *A* by loops. Because of the presence of the defects, which contain disconnected hydrophilic units of the electrostatically complementary chains, the S-PEC swell appreciably in water. The hydrophobic ladder sections limit the capacity of the S-PEC for swelling in aqueous media. The non-polar interactions of these units with one another lead to the compaction of the PEC species in dilute aqueous solutions[28,29]. The electron micrograph in Fig.2 illustrates typical globular PEC particles formed as a result of the reaction between poly-L-lysine and polyacrylic acid (PAA) in a dilute aqueous solution. Structures of this type were first discovered in 1959.[30] The coiling of the S-PEC species into compact globules is possible by virtue of the marked bending of the two-stranded formations at the sites of the defects (loops).

The presence of defects in the products of the completed reactions can be due to different causes. One of these is the "freezing" of the random intermolecular contacts arising in the early stages of the rapid ionic reaction. After the deposition of the PEC, its subsequent rearrangement, tending to "heal" the defects, probably proceeds very slowly. Thus certain non-equilibrium states are fixed in the system. This is indicated by data obtained in studies[28,29] in which the relaxation of the PEC formed as a result of the neutralisation of strong polymeric acids by strong polymeric bases was observed. On the other hand, if the conditions for the occurrence of non-equilibrium structures are excluded, for example, by employing matrix polymer reactions for the preparation of the PEC, then the resulting PEC can prove to be highly ordered[31-33].

However, in the general case one has to bear in mind also another important factor determining the defectiveness of the PEC: the absence of a steric correspondence between the electrostatically complementary chains. The majority of the PEC described in the literature are products of the interaction of sterically irregular macromolecules. Such PEC are amorphous as regards X-ray diffraction and contain at least 20–30% of pairs of disconnected units, i.e. units incorporated in defects. This is demonstrated convincingly by the results of the study of ion-exchange equilibria with a series of different PEC.[34] Even in the product of the complete reaction between linear polyethyleneimine (PEI) and atactic PAA, whose chains are characterised by a fairly satisfactory steric correspondence, 20% of the units of each type are in the defects. The infrared spectra of the PEC dialysed against water indicate the presence of ~20% of protonated carboxy-groups[35]. On the other hand, the two-stranded ladder sections in such PEC have an extremely ordered structure. This is indicated by the fact that, in the products of the interaction of PAA and PEI in the vitreous state, the intermolecular salt bonds are quantitatively converted into covalent amide bonds at elevated temperatures[35-37]:



(II)

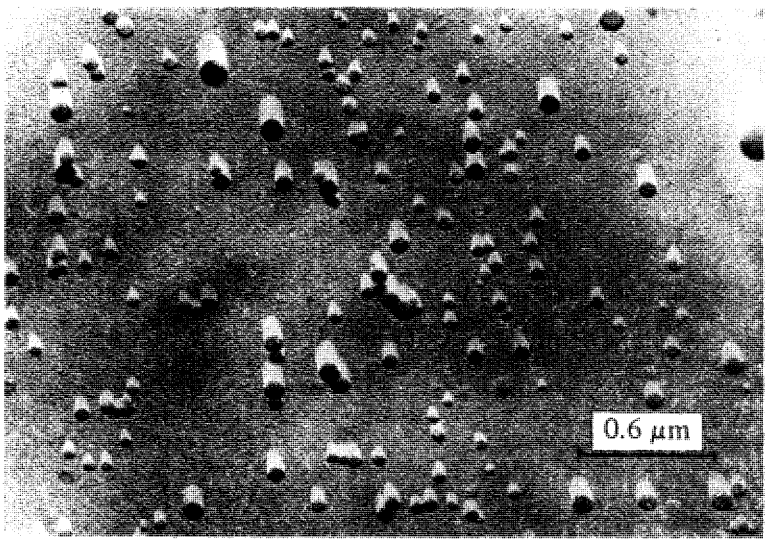
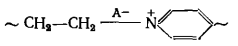


Figure 2. Photomicrograph of particles of the stoichiometric PEC formed as a result of the reaction between equivalent amounts of poly-L-lysine and polyacrylic acid at pH 4.2 and a concentration of polyelectrolytes of 10^{-5} basic M.[29]

The units located in the defects do not enter into this reaction.

The foregoing does not imply that the presence of a considerable number of defects is characteristic of all the PEC obtained by the direct mixing of solutions of electrostatically complementary polyelectrolytes. Crystalline PEC, i.e. low-defect PEC, obtained, for example, from ionene, which is a product of the 1,4-polymerisation of 4-vinylpyridine,

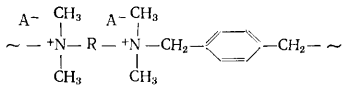


and isotactic PAA [38] and also from ionene and a polyphosphate (PP),[39] have been described in the literature. However, presumably the stereoregularity and the satisfactory steric correspondence of the initial components are essential conditions for the formation of highly-ordered crystalline PEC.

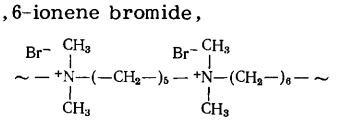
III. SYNTHESIS OF WATER-SOLUBLE NON-STOICHIOMETRIC POLYELECTROLYTE COMPLEXES

In contrast to the S-PEC, the history of the study of which covers a period of approximately 20 years as already mentioned, detailed and systematic studies of the N-PEC began less than 10 years ago. The publications by Tsuchida et al.[40] and Gulyaeva et al.[41] are some of the first in which N-PEC were described. The ability of the N-PEC to dissolve in aqueous media was noted as their main characteristic in the above publications.

Tsuchida et al.[40] were the first to describe in detail the procedures for the preparation of non-stoichiometric water-soluble PEC. They showed that N-PEC are formed as a result of the mixing of aqueous solutions of aromatic ionenes



and sodium polystyrenesulphonate (PSS-Na) taken in non-equivalent proportions. It was observed that the PEC dissolve only when PSS-Na is present in excess relative to ionene. The complete dissolution of the PEC is observed in the presence of a threefold excess of PSS-Na. When excess amounts of ionene are introduced into PSS-Na solutions, a soluble PEC is not formed. In the latter case, insoluble S-PEC is produced and excess ionene remains in solution. These observations led the authors[40] to the conclusion that polymers of the series of ionenes have a special ability to form soluble PEC, which in their view is associated with the localisation of the charged groups in the chain of the main valences of the macromolecules. The authors[40] were unable to obtain water-soluble PEC from PSS-Na and polybenzylvinyltrimethylammonium chloride, i.e. from polyelectrolytes in which the ionogenic groups are localised in the side-substituents. It was soon shown[41], in relation to the reaction between the sodium polyacrylate (PA-Na) and 5,6-ionene bromide,



that aliphatic ionenes are also capable of forming water-soluble N-PEC. The above facts are seemingly consistent with the hypothesis of the exceptional properties of ionenes which, if one follows the reasoning of Tsuchida et al.[40], are due to the steric "accessibility" of the positively charged quaternary nitrogen atoms.

However it was shown later[42–45] that water-soluble N-PEC can be obtained from oppositely charged polyelectrolytes of a wide variety of chemical structures when certain conditions are observed. The examples of the water-soluble N-PEC known at present are presented in Table 1. Evidently N-PEC can be formed by pairs of strong polyelectrolytes, pairs of weak polyelectrolytes, and by mixed pairs. It is also seen that N-PEC can be obtained by the reaction of two electrostatically complementary polyelectrolytes in each of which the charged compounds are localised in the side-substituents and not in the chain of the main valences of the macromolecule, for example, PA-Na–poly(dimethylaminoethyl methacrylate) hydrochloride (PDMAEMA.HCl) or PA-Na–poly-*N*-ethyl-4-vinylpyridinium bromide (PVP.C_2H_5Br). The polyelectrolyte incorporated in the N-PEC in excess can be both negatively and positively charged. It follows from Table 1 that the structural-chemical limitation introduced by Tsuchida[40] is erroneous. As will be shown later, the necessary and sufficient conditions for the formation of soluble N-PEC are not associated directly with the chemical structure of the units of the electrostatically complementary polyelectrolyte components.

Table 1. Non-stoichiometric polyelectrolyte complexes and methods for their preparation[41,42].

LPE	BPE	Examples	Methods of preparation
s. (–)	s. (+)	PP-ionenes	*a'*, *a''*
s. (–)	s. (+)	heparin-ionenes	*a'*, *a''*
s. (–)	s. (+)	PSSA-ionenes	*a'*, *a''*
s. (–)	s. (+)	PSSA-PVP.C_2H_5Br	*a'*, *a''*
s. (–)	w. (+)	PP-PDMAEMA	*a'*, *a''*
w. (–)	s. (+)	PAA-ionenes	*a'*, *a''*, *b'*
w. (–)	s. (+)	PAA-PVP.C_2H_5Br	*a'*, *a''*, *b'*
w. (–)	s. (+)	PMAA-ionenes	*a'*, *a''*, *b'*
w. (–)	s. (+)	PMAA-PVP.C_2H_5Br	*a'*, *a''*, *b'*
w. (–)	w. (+)	PAA-PDMAEMA	*a'*, *a''*, *b'*
w. (–)	w. (+)	PAA-PEI	*a'*, *a''*, *b'*
w. (–)	w. (+)	PMAA-PEI	*a'*, *a''*, *b'*
s. (+)	s. (–)	ionenes-PP	*a'*, *a''*
s. (+)	w. (–)	PVP.C_2H_5Br-PMAA	*a'*, *a''*
w. (+)	s. (–)	PDMAEMA-PP	*a'*, *a''*, *b''*
w. (+)	s. (–)	PDMAEMA-heparin	*a'*, *a''*, *b''*
w. (+)	s. (–)	PDMAEMA-lignosulphonate	*a'*, *a''*, *b''*
w. (+)	w. (–)	PDMAEMA-PAA	*a'*, *a''*, *b''*
w. (+)	w. (–)	PDMAEAA-PMAA	*a'*, *a''*, *b''*

Notation: LPE and BPE are the lyophilising and blocking polyelectrolytes; s.(–), s.(+), and w.(+) are respectively strong and weak polyelectrolytes charged negatively and positively; PMAA = polymethacrylic acid; the notation used for the other polyelectrolytes and for the methods of preparation of the PEC is described in the text.

The data permitting the formulation of one of the necessary conditions for the formation of water-soluble N-PEC were first obtained by Kasaikin et al.[43]. In the synthesis of N-PEC, non-equivalent amounts of the initial polyelectrolyte components are introduced into the reaction. We shall adopt the convention that the overall condition of the reaction system is henceforth characterised by the quantity Z, which represents the ratio of the concentration of the units of the component present in a deficient amount to the concentration of the units of the component present in excess. Kasaikin[43] presents data for the solubilities of

the products of the interpolymer reaction in the PDMAEMA.HCl–sodium polyphosphate (PP-Na) system# as a function of the degree of polymerisation of the initial components P.

It follows from these data that the soluble products are formed only for $\bar{P}_1/\bar{P}_2 \gtrsim 1$. In all cases the reaction conditions correspond to a virtually complete shift of equilibrium (Ib) to the right, i.e. the degree of conversion θ, calculated with respect to the component present in a deficient amount, is close to unity. Consequently the soluble product is an N-PEC with the composition Z. If $\bar{P}_1 < \bar{P}_2$, the reaction product precipitates; analysis of the compositions of the coexisting phases showed that the precipitate is an S-PEC which incorporates the entire deficient polyelectrolyte. Only the superstoichiometric amount of the polyelectrolyte component introduced in excess remains in solution.

A completely analogous situation is observed in the same system with the "reverse" ratio of the PDMAEMA.HCl and PP-Na concentrations with an excess of polyanions instead of polycations. In this system N-PEC is formed only for $\bar{P}_1 > \bar{P}_2$. However, this requirement implies that the polyanions introduced in excess must be longer than the polycations[43].

Turning again to the studies[40,41,44] in which the N-PEC were first described, one should note that the condition $\bar{P}_1 > \bar{P}_2$ was in fact observed, since the N-PEC were obtained when the high-molecular-weight polyanions predominated over the relatively low-molecular-weight polycations (ionenes).

Thus the necessary condition for the formation of the N-PEC, concerning the ratio of the degrees of polymerisation of the electrostatically complementary polyelectrolyte pairs, is $\bar{P}_1 \geq \bar{P}_2$. To facilitate further exposition, we shall now introduce certain new definitions and characteristics. The relatively high-molecular-weight component present in the N-PEC in excess will be referred to as the lyophilising polyelectrolyte (LPE)§. The relatively low-molecular-weight component present in the N-PEC in a deficient amount will be called the blocking polyelectrolyte (BPE)¶.

Thus, by definition, the degree of polymerisation of the LPE ($\bar{P}_{LPE}$) is always greater than or equal to the degree of polymerisation of the BPE ($\bar{P}_{BPE}$). The composition of the N-PEC will be expressed in terms of the ratio of the number of units in the BPE to the number of units in the LPE incorporated in the N-PEC, designated by $\phi = [BPE]/.[LPE]$. Evidently ϕ can vary from 0 to 1. If the PEC is the product of a completed reaction, i.e. corresponds to $\theta \cong 1$ (such PEC will in fact be considered henceforth), the limiting value $\phi = 1$ corresponds to the transformation of the N-PEC into the S-PEC. Naturally $\phi = 0$ corresponds to a solution of the free LPE.

The condition $\bar{P}_1 \geq \bar{P}_2$ formulated above is insufficient for the formation of N-PEC on direct mixing of salt-free dilute aqueous solutions of oppositely charged polyelectrolytes. It is also necessary that the solution in which the reaction is carried out contains a certain amount of a low-molecular-weight electrolyte. This amount may be comparatively small. The required concentration of the 1:1-valent electrolyte, for example NaCl, can vary in the range 0.002–0.12 M, depending on the chemical nature of the polyelectrolytes and their ratio in the system. Generally speaking, the greater the excess of the high-molecular-weight component, i.e. the lower the value of Z, the lower the concentration of the low-molecular-weight salt necessary for the formation of the water-soluble N-PEC (Fig.3).

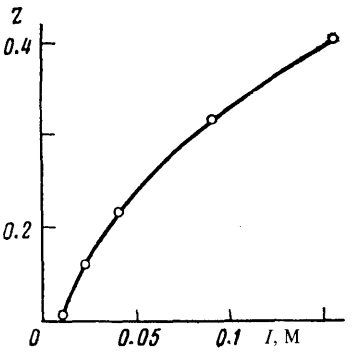


Figure 3. Dependence of the composition of a mixture of polyelectrolytes for which N-PEC dissolves in the sodium polymethacrylate (PMA-Na)–poly-*N*-ethyl-4-vinylpyridinium bromide (PVP.C_2H_5Br) system on the ionic strength of the solution I.[42]

For the complete dissolution of the product of the completed reaction between the BPE and the LPE, it is also necessary that their ratio in the system should not exceed a characteristic value: $Z \leq Z_{char}$. The characteristic composition of the N-PEC ($\phi_{char} = Z_{char}$) corresponds to this condition. If $Z > Z_{char}$, then the dissolved N-PEC with the characteristic composition ϕ_{char} and the corresponding amount of the insoluble S-PEC coexist in the reaction system. The value of ϕ_{char} for the majority of the systems studied varies in the range from 0.5 to 0.2 and depends mainly on the chemical nature of the polyelectrolytes constituting the PEC. It is still not altogether clear what determines the value of ϕ_{char}, but it presumably depends to a large extent on the steric correspondence of the units of the BPE and the LPE and also on the degree of hydration of the intermacromolecular salt linkages and the degree of binding of small counterions to the units of the LPE incorporated in excess in the PEC.

We shall now consider the specific procedures for the preparation of N-PEC. A general method for different pairs of polyelectrolytes whereby N-PEC can be synthesised consists in the direct mixing of solutions of fully ionised oppositely charged polyelectrolytes taken in appropriate proportions ($Z \leq Z_{char}$) and containing the necessary amounts of a low-molecular-weight salt (composition *a* in Table 1); such mixing can be achieved in two ways.

#Here and henceforth in the designation of the polyelectrolyte systems investigated we shall first indicate the component present in excess.

§In publications in English, for example in the book by Kabanov et al.[47], the term host-polyelectrolyte has also been adopted for LPE.

¶In the original publications[42,43,46,52,55] the BPE has also been called the reference polyelectrolyte and, in publications in English, the "guest-polyelectrolyte".[47]

Procedure *a'* consists in the gradual addition of a solution of the LPE to a solution of the BPE. The polyelectrolyte chosen as the LPE is then initially present in a deficient amount relative to the BPE. According to the above considerations, in this stage the N-PEC is not formed, since the reaction system is characterised by a ratio of the degrees of polymerisation of the reactants unfavourable for the formation of the N-PEC. Instead an insoluble S-PEC is formed and accumulated and the solution of the polyelectrolyte chosen as the BPE is in equilibrium with it. Fig.4*a* presents curves for the turbidimetric titration of a solution of 5,6-ionene bromide (BPE) with a solution of PP-Na (LPE) and for the titration of a solution of PP-Na (BPE) with a solution of PDMAEMA.HCl (LPE). The increase of turbidity with change in the composition of the mixture of polyelectrolytes is linear and corresponds to the accumulation of the insoluble S-PEC. The maximum turbidity corresponds to the equivalent proportions of the polyelectrolytes in the system ($Z = 1$). At the maximum both polyelectrolytes are quantitatively incorporated in the insoluble S-PEC. A further increase of the amount of the high-molecular-weight component chosen as the LPE is accompanied by a gradual, virtually linear decrease of turbidity.

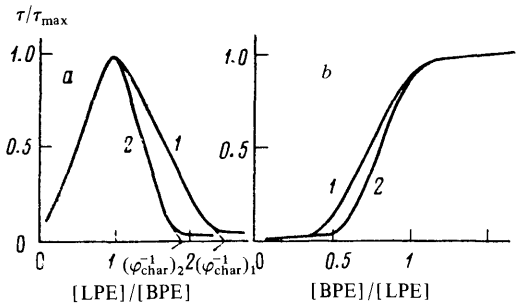


Figure 4. Turbidimetric titration curves: *a*) titration of an aqueous solution of 5,6-ionene bromide (BPE, $\bar{M}_w = 1.4 \times 10^4$) with a solution of PP-Na (LPE, $\bar{M}_w = 6.6 \times 10^4$) at pH 7.0 in 0.01 M NaBr (curve *1*) and of an aqueous solution of PP-Na (BPE, $\bar{M}_w = 1.7 \times 10^4$) with a solution of PDMAEMA.HCl (LPE, $\bar{M}_w = 6.3 \times 10^5$) at pH 4.5 in 0.1 M NaCl (curve *2*); *b*) ditto with the reverse order of mixing of the solutions; τ_{max}—maximum turbidity of the system[47].

Analysis of the composition of the coexisting phases shows that the concentrated phase contains the stoichiometric PEC. Its amount diminishes with increase of the excess of the LPE. The N-PEC accumulates in the dilute solution; its composition remains unaltered up to the complete dissolution of the precipitate and is specified by ϕ_{char}. The reciprocal ϕ^{-1}_{char} in Fig.4*a* corresponds to the intercept which the descending branch of the curve makes on the abscissa axis. Thus the procedure for the preparation of the N-PEC examined above virtually consists in the dissolution of the S-PEC under the influence of the excess of the LPE, i.e. in the transformation of the S-PEC into the N-PEC.

The second procedure (*a''*) leading to the preparation of the N-PEC consists in the addition of a solution of the BPE to that of the LPE. Fig.4*b* presents the corresponding turbidimetric titration curves for the same polyelectrolyte salt as in Fig.4*a*. Evidently the initial section of the curve corresponds to the homogeneous system. This is natural, since, in the given range of compositions of the polyelectrolyte mixtures, the condition $\bar{P}_1 > \bar{P}_2$, necessary for the formation of the soluble N-PEC, is satisfied; the LPE is present in excess at this stage. The system remains homogeneous over the entire range of compositions of the reaction mixture for $Z \leqslant Z_{char}$. Depending on the ratio $\bar{P}_{LPE}/\bar{P}_{BPE}$, the composition of the N-PEC can either vary within wide limits or can remain unaltered. The causes of this will be examined at the end of this Section.

A further alteration of the composition of the polyelectrolyte mixture is accompanied by the appearance and accumulation of a deposit of the S-PEC (up to $Z = 1$). In the range $Z_{char} < Z \leqslant 1$, the insoluble S-PEC coexists with the soluble N-PEC having the characteristic composition. Following the attainment of $Z = 1$, both polyelectrolytes are quantitatively incorporated in the particles of the insoluble S-PEC, after which further addition of the BPE no longer leads to such appreciable changes in the state of the system. The excess BPE simply accumulates in the solution. In this range of compositions the formation of the N-PEC is impossible, since we now have $\bar{P}_1 < \bar{P}_2$. In contrast to the previous method, this procedure presupposes the formation of the N-PEC in a homogeneous system and allows for the possibility of varying the composition of the N-PEC over a wide range.

The procedures described above consist in carrying out the reaction between wholly or almost wholly dissociated LPE and BPE taken in considerable proportions. The N-PEC are then formed immediately as products of the completed reactions ($\theta \cong 1$). However, other procedures are also possible whereby the N-PEC can be obtained from weak polyelectrolytes. They are based on the ability of pairs of polyelectrolytes, at least one of which is weak, to form the N-PEC for $\theta \ll 1$, i.e. under conditions where the interpolymer reaction is far from completion. Such N-PEC can be both soluble and insoluble in water. Insoluble S-PEC, formed in acid media by the reaction of PAA and polymethacrylic acid (PMAA) with various polymeric bases, have been described[24,44]. The virtually unionised units of the polymeric acid are incorporated in the N-PEC species in a 2–5-fold excess. It has been suggested that the solubility of these N-PEC is due to the compaction of their species. The compact conformations are stabilised by the hydrogen bonds formed by the excess carboxy groups. Non-polar interactions also play an important role in the stabilisation of these compounds.

Fig.5 presents curves for the potentiometric and turbidimetric titration of the PMAA–PVP.C_2H_5Br system with alkali (NaOH) for $Z = 0.2$. The degrees of neutralisation of the PMAA (α), calculated relative to the entire polymeric acid introduced into the reaction with the polycation, are plotted along the abscissa axis. The reaction product formed on mixing aqueous solutions of the polycation and free PMAA taken in a 5-fold excess was considered as the initial system. This reaction is accompanied by the liberation of protons into the solution [equilibrium (Ia)] and the formation of an insoluble N-PEC. Both polyelectrolytes are quantitatively incorporated in the species of the polymeric complex[45]. However, only ~25% of the units of the polycations functioning as the BPE form salt linkages with the macromolecules of the polymeric acid in the N-PEC formed. If alkali (for example, NaOH) is now added to the colloidal dispersion obtained, the reaction involving the formation of salt linkages between the BPE and the LPE is initially completed. The degree of ionisation of the PMAA then varies in the range between 0 and 0.2; at the same time there is a

slight increase of the pH to ~4, which is accompanied by an increase of the turbidity of the system. For $\alpha = 0.2$, an N-PEC in which virtually all the quaternary nitrogen atoms form salt linkages with an equivalent number of the charged carboxy-groups of the PMAA ($\theta \cong 1$) exists in the system.

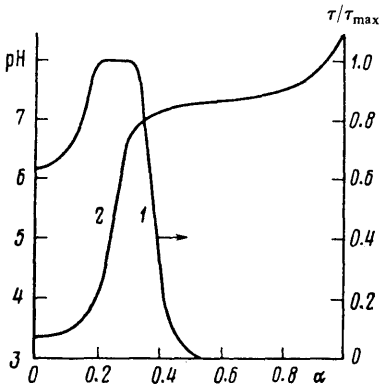


Figure 5. Curves for turbidimetric (curve *1*) and potentiometric (curve *2*) titration of an acid solution of a mixture of polymethacrylic acid (PMAA) (LPE, $\bar{M}_w = 2.6 \times 10^5$) and PVP.$C_2H_5Br$ (BPE, $\bar{M}_w = 2 \times 10^5$) having the composition $Z = 0.2$ with sodium hydroxide; [PVP.C_2H_5Br] = 2×10^{-3} basic M; α = degree of neutralisation[45].

However, such N-PEC is still insoluble in water, because the free PMAA units functioning as the LPE are not yet ionised and they do not therefore exhibit an adequate lyophilising capacity. The subsequent addition of alkali leads to the ionisation of the free carboxy-groups of the PMAA incorporated in excess in the N-PEC. After the attainment of $\alpha \cong 0.5$, the N-PEC dissolves. This follows from the form of the turbidimetric titration curve. On the other hand, the potentiometric titration curve exhibits a sharp rise, showing that the dissolution of the N-PEC is accompanied by a conformational transformation of its species: the compact conformations are converted into the uncoiled conformations characteristic of charged macromolecular chains. The degree of ionisation of the LPE necessary for the dissolution of the N-PEC is higher the smaller the excess of the LPE in the N-PEC species, i.e. the higher the value of ϕ. The dissolution of the N-PEC having the characteristic composition requires virtually complete charging of the units of the LPE chains. The method for the preparation of water-soluble N-PEC described above will henceforth be designated by *b'*.

An analogous procedure can be used also in cases where weak polymeric bases are used as the LPE. An example is provided by the PDMAEMA.HCl–PP-Na system[42]. When solutions of the polymeric components are mixed in an alkaline medium, where the amino-groups of the LPE are uncharged, the N-PEC formed initially is a product of the uncompleted reaction (but this time it is soluble). In the course of the subsequent titration of the reaction mixture with acid (HCl), the degree of completion of the interpolymer reaction θ increases to a value close to unity, but the excess free amino-groups of the LPE are still not protonated and the N-PEC formed in the intermediate titration range is precipitated. However, further addition of the acid leads to the charging of the free amino-groups of the LPE and to the formation of a soluble N-PEC. This method for the preparation of water-soluble N-PEC will be designated by *b''*.

Thus water-soluble N-PEC can be obtained in several ways. The possibility therefore arises of the solution of the fundamentally important problems of whether the water-soluble N-PEC are equilibrium compounds, i.e. whether their state depends on the way in which they have been obtained. In order to answer this question, it is necessary to compare the characteristics of the N-PEC formed by the same pair of polyelectrolytes having a fixed composition but prepared in different ways. Table 2 presents the weight-average molecular weights $\bar{M}_w$, the mean-square radii of inertia $(\bar{R}_g^2)^{1/2}$, the second virial coefficients of the solution A_2 obtained by the light scattering method, and the sedimentation coefficients S. It follows from Table 2 that the above characteristics of each of the N-PEC investigated are almost independent of the method of preparation. Consequently the soluble N-PEC must be regarded as equilibrium macromolecular compounds, which implies, in particular, that the methods widely used to investigate the usual polymer solutions, especially solutions of polyelectrolytes, can be employed for their investigation.

Table 2. Characteristics of the water-soluble non-stoichiometric PEC prepared by different methods[42].

PEC	Method	I, M	pH	$10^{-5}\bar{M}_w$	$(\bar{R}_g^2)^{1/2}$, Å	$10^4 \cdot A_2$	S
PA-Na-5,6-ionene	*a'*	0.025	7.2	3.80	300	0.18	—
ditto	*a''*	0.025	7.2	3.30	300	0.20	—
»	*b'*	0.025	7.2	3.30	260	0.17	—
PDMAEMA.HCl-PP	*a'*	0.100	4.0	7.70	390	2.9	5.8
ditto	*a''*	0.100	4.0	7.70	380	3.3	5.4
»	*b''*	0.100	4.0	7.20	370	2.8	5.5
PP-Na-5,6-ionene	*a'*	0.025	7.0	0.77	—	0.16	—
ditto	*a''*	0.025	7.0	0.77	—	0.15	—
PMA-Na-PVP.C_2H_5Br*	*a'*	0.125	7.5	12.50	420	1.1	—
ditto	*b'*	0.125	7.5	12.50	410	1.3	—
PDMAEMA.HCl-PAA	*a'*	0.100	4.5	5.60	435	8.6	3.2
ditto	*a''*	0.100	4.5	—	—	—	3.3
»	*b''*	0.100	4.5	—	—	—	3.2

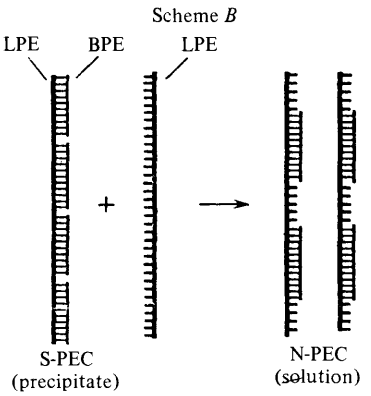
*$\phi = 0.25$; in the remaining cases $\phi = 0.33$.

Remarks: I = ionic strength of the solution; S = sedimentation coefficient (in Svedberg units) determined at a fixed concentration of the N-PEC (0.28 wt.%).

It was already noted above that in the reactions between polyelectrolytes, there is a possibility of the formation of both insoluble S-PEC and soluble N-PEC. Such situations are also observed when an insoluble S-PEC coexists with an N-PEC solution. It is significant that the characteristic composition of the N-PEC (ϕ_{char}) differs considerably from that of the stoichiometric polyelectrolyte. It has also been shown that, when an LPE is added to the S-PEC, the entire PEC gradually dissolves in the form of the N-PEC having

the characteristic composition[41]. In the case where $\bar{P}_{LPE} \gg \bar{P}_{BPE}$, this process can be represented by Scheme *B*.

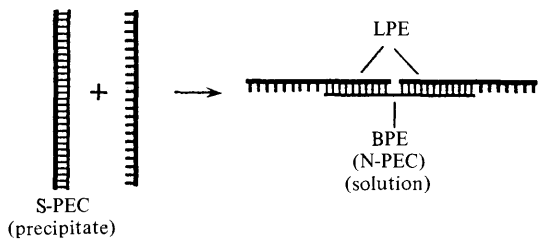
Scheme *B*



It must be supposed that the driving force of the spontaneous formation of the water-soluble N-PEC after the addition of the LPE is the increase of the entropy of the system by virtue of the additional increase of the number of species in solution compared with the number of the LPE molecules introduced. The number of intermolecular salt linkages then remains unaltered.

However, the increase in the number of species in solution is apparently not the only factor determing the conversion of the insoluble S-PEC into the soluble N-PEC. This transformation occurs also when the degrees of polymerisation of the polyelectrolyte components are similar ($\bar{P}_1 \cong \bar{P}_2$), although the number of N-PEC species formed in this situation cannot exceed the number of macromolecules of all of the components added in excess to the system containing the S-PEC. The formation of the water-soluble N-PEC for $\bar{P}_1 \cong \bar{P}_2$ can be represented by Scheme *C*.

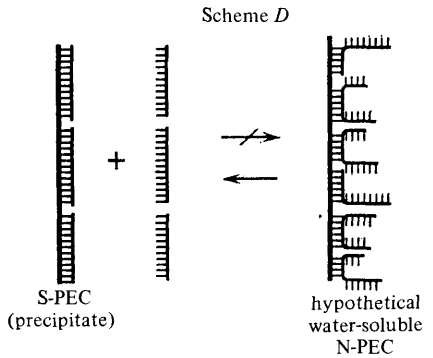
Scheme *C*



The number of interpolymer salt linkages remains unchanged after this transformation, as in the preceding case. However, reaction *C* can still be accompanied by an increase of the entropy of the system due to the transfer of the defects present both in the S-PEC and in the N-PEC from the precipitate to the solution. It was stated above that these defects, not illustrated in Schemes *B* and *C*, consist of loops made up of sequences of disconnected units of the electrostatically complementary chains (see Scheme *A*). The transfer of such loops from the concentrated to the dilute phase can be accompanied by an increase of the entropy of mixing of the system. The latter factor must naturally be taken into account also in considering processes described by Scheme (III). We may note that, for water-soluble N-PEC formed by chains with a similar degree of polymerisation, the concept of the LPE and BPE becomes degenerate. In this case the polyelectrolyte component present in excess actually plays the role of the LPE.

Finally, we shall consider the question why the water-soluble N-PEC are not formed when $\bar{P}_1 < \bar{P}_2$, i.e. why the excess of a polyelectrolyte having relatively short chains cannot lyophilise the oppositely charged long-chain polyelectrolyte. If one takes into account the fact that the PEC species acquires the ability to dissolve in the form of N-PEC only when its composition includes a considerable (at least two-fold) excess of LPE units, then the case under consideration may be reduced to Scheme *D*.

Scheme *D*



Evidently, the formation of the hypothetical N-PEC should result in a considerable decrease in the number of species in solution and the decrease should be greater the lower the degree of their polymerisation. When the total number of intermolecular salt contacts remains unchanged, this should be accompanied by a considerable decrease of the entropy of the system. Consequently process *D* can occur only from right to left, i.e. its occurrence from left to right is thermodynamically prohibited. An illustration of this situation is provided by the solubilities of the PEC and also the data in Fig.4*b*. It follows from Fig.4*b* that the introduction of an excess of the BPE into the reaction system relative to its content in the N-PEC for $\phi = \phi_{char}$ is accompanied by the formation of the S-PEC, which precipitates. After the attainment of the overall system composition $Z = 1$, a further addition of the BPE does not lead to any changes in the state of the insoluble S-PEC formed. The excess BPE simply accumulates in the solution over the precipitate.

Evidently the exact boundary between the polyelectrolyte pairs which are and are not capable of forming water-soluble N-PEC cannot be established exactly by an experimental procedure using only the average degrees of polymerisation of the electrostatically complementary polymeric components. This is due to the finite width of the molecular weight distribution of the fractions employed in the experiment. However, on the basis of the experimental data and their interpretation presented above, one can assume with an adequate degree of approximation that this boundary is in fact close to the ratio $P_1/P_2 = 1$. We may note that in all the examples considered the overall compositions Z were finite. One cannot rule out the possibility that, when a very large excess of even a relatively low-molecular-weight polyelectrolyte is used, it is possible to observe the spontaneous dispersion and peptisation of the PEC. However, the nature of such phenomena must be different and their consideration is outside the scope of our task.

In conclusion of this Section, we shall consider the question of the influence of the ratio $\bar{P}_{LPE}/\bar{P}_{BPE}$ on the characteristics of the compositions of the N-PEC formed. For this, it is sufficient to investigate two limiting cases: $\bar{P}_{LPE}/\bar{P}_{BPE} \gg 1$ and $\bar{P}_{LPE}/\bar{P}_{BPE} \cong 1$.

We shall consider the system PDMAEMA.HCl (LPE)–PA-Na (BPE). In the first of the versions investigated $\bar{P}_{LPE} = 3200$ and $\bar{P}_{BPE} = 150$, i.e. $\bar{P}_{LPE}/\bar{P}_{BPE} = 21 \gg 1$. Fig.6*a* presents sedimentation diagrams for mixtures of the above polyelectrolytes in the composition range $0.13 < Z < 0.5$ and also for free LPE. Evidently the peaks on the sedimentation

diagrams are symmetrical and fairly narrow, which indicates the inhomogeneity of the species of the water-soluble N-PEC as regards composition. The sedimentation coefficient S of the N-PEC decreases appreciably with decrease of the relative content of the BPE in the polymeric complex, i.e. as ϕ diminishes. When ϕ becomes sufficiently small ($\phi < 0.1$), the sedimentation coefficients of the N-PEC and LPE hardly differ. Thus, in systems where $\bar{P}_{LPE}/\bar{P}_{BPE} \gg 1$, the composition of the water-soluble N-PEC can be varied within fairly wide limits. The composition of the N-PEC then agrees with the overall composition of the mixture of polyelectrolytes, i.e. it can be readily specified in the experiments. The range of variation of the composition of the water-soluble N-PEC is determined by the inequality $\bar{P}_{BPE}/\bar{P}_{LPE} < \phi < \phi_{char}$.

In the second version $\bar{P}_{LPE} = 3200$ and $\bar{P}_{BPE} = 3500$ in the same system, i.e. $\bar{P}_{LPE}/\bar{P}_{BPE} \cong 1$. Fig.6*b* presents the corresponding sedimentation diagrams. Evidently the water-soluble N-PEC with the compoistion $\phi = 0.5$, which is the characteristic composition, is sedimented as an individual compound. The sedimentation diagrams show only a single peak whose sedimentation coefficient is significantly higher than the sedimentation coefficients of each of the initial components. A further enrichment of the system in PDMAEMA.HCl (LPE) leads only to its accumulation in the solution in a free state. This is evident from the appearance of a second peak on the sedimentation diagram, which corresponds to free PDMAEMA.HCl. Some decrease of the sedimentation coefficients of the excess polyelectrolyte with increase of its concentration in solution as well as the decrease of the sedimentation coefficient of the N-PEC are due to the increase of the viscosity of the medium. The area of the slowly sedimenting PDMAEMA.HCl peak steadily increases with increased content of this component in the system, i.e. with decrease of Z. Thus, in systems made up of polyelectrolytes having similar degrees of polymerisation, there is a possibility of the formation of only the N-PEC having the characteristic compositions ϕ_{char}. Variation of the overall system composition Z leads in this case to the appearance and accumulation in solution of an excess of the LPE which coexists with the N-PEC having the characteristic composition.

The behaviour, described above, for mixtures of oppositely charged polyelectrolytes having different ratios of degrees of polymerisation, is characteristic of an extremely wide range of polyelectrolyte pairs[43]. Thus one may conclude that, when $\bar{P}_{BPE}/\bar{P}_{LPE} < \phi_{char}$, the range of variation of the composition of the water-soluble N-PEC is determined by the inequality $\bar{P}_{BPE}/\bar{P}_{LPE} < \phi < \phi_{char}$. Evidently the composition of the species of the water-soluble N-PEC varies discretely with the overall mixture composition in the above range of ϕ by the amount $\bar{P}_{BPE}/\bar{P}_{LPE}$ or its multiple. On the other hand, if $1 \geq \bar{P}_{BPE}/\bar{P}_{LPE} > \phi_{char}$, then N-PEC with the characteristic composition only is always formed regardless of the overall mixture composition.

The above data on the methods of preparation of water-soluble N-PEC and the compositions of these macromolecular compounds are necessary for the correct choice of conditions in which their structures and properties can be usefully investigated.

IV. STRUCTURE OF WATER-SOLUBLE NON-STOICHIOMETRIC POLYELECTROLYTE COMPLEXES

In the first place we shall consider data obtained by light scattering[46,47]. We may note that solutions containing a single macromolecular component, namely N-PEC, have always been investigated. As stated above, in order to achieve this, the compositions of the corresponding polyelectrolyte mixture must satisfy the condition $\bar{P}_{BPE}/\bar{P}_{LPE} < Z < \phi_{char}$. The sedimentation diagrams for such mixtures are characterised by the presence of a single peak corresponding to the N-PEC. As a rule, light scattering measurements have been carried out in aqueous salt media (concentration of the low-molecular salt not less than 0.1 M) in order to suppress the polyelectrolyte effect. In order to be able to reduce the analysis of the experimental results to a canonical consideration of two-component polymer–solvent systems, in each series of experiments the activity of the low-molecular-weight salt in solutions of the N-PEC at different concentrations was kept constant. This was achieved by dialysing N-PEC in solution at different experimental concentrations against the same aqueous salt solution. The increment in the refractive index $(\partial n/\partial c)_I$ at an ionic strength I was measured making sure that the same requirements were satisfied[48].

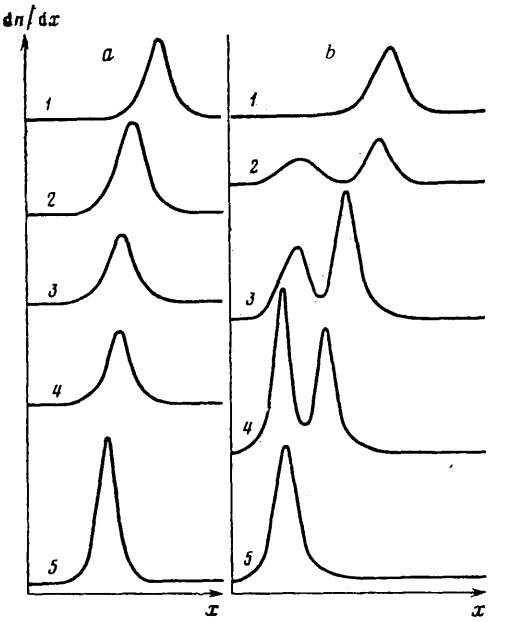


Figure 6. Sedimentation diagrams for mixtures of polyelectrolytes: *a*) PDMAEMA.HCl (LPE, $\bar{P} = 3.2 \times 10^3$) and PA-Na (BPE, $\bar{P} = 1.5 \times 10^2$) with different compositions Z [*1*) 0.5; *2*) 0.33; *3*) 0.2; *4*) 0.13; *5*) 0]; concentration of solutions 0.35 wt.%; time 100 min for a rate of rotation of rotor of 5600 min^{-1}; *b*) PDMAEMA.HCl (LPE, $\bar{P} = 3.2 \times 10^3$) and PA-Na (BPE, $P = 3.5 \times 10^3$) with different compositions Z [*1*) 0.4; *2*) 0.33; *3*) 0.2; *4*) 0.13; *5*) 0]; concentration of solutions 0.28 wt.%; time 70 min for a rate of spinning of 56000 min^{-1}. All the experiments were performed at pH 5.0 in 0.1 M NaCl at 20 °C.[43]

Fig.7 presents typical Zimm diagrams for N-PEC solutions obtained in the PDMAEMA.HCl–PP-Na systems for different ratios of the polyelectrolyte components. Evidently the double extrapolation plots do indeed have the form characteristic of normal polymer solutions. The relations between $(Kc/R_\theta)_\theta$ and c and between $(Kc/R_\theta)_c$ and $\sin^2(\theta/2)$ are

linear, which indicates the absence of polyelectrolyte swelling and dissociation of the N-PEC species into the initial components when the solutions are diluted.

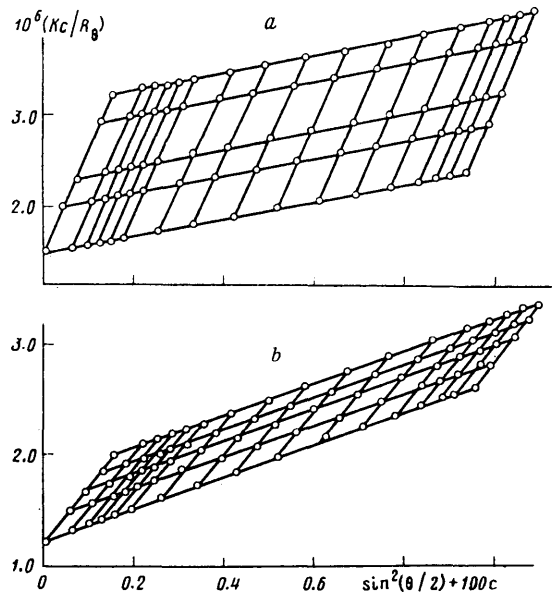


Figure 7. Zimm diagrams for solutions of the PDMAEMA.HCl ($\bar{M}_w = 6.3 \times 10^5$)–PP ($\bar{M}_w = 1.7 \times 10^4$) N-PEC at pH 4.0 in 0.1 M NaCl for different compositions ϕ: *a*) 0.13; *b*) 0.33.[46]

Table 3 presents the weight-average molecular weights $\bar{M}_w$ of a series of N-PEC having a fixed composition ϕ measured by the light scattering method. For comparison, the Table also includes the calculated molecular weights. In the calculation it was assumed that the N-PEC species have homogeneous compositions and that each contains only one LPE macromolecule and that the number of BPE macromolecules corresponds to the composition ϕ. Account was taken also of the fact that the formation of a single salt linkage between the LPE and BPE units is accompanied by the liberation of a pair of small ions present in solutions of the initial component as counterions. The degree of conversion θ relative to the BPE in the reaction involving the formation of the N-PEC was assumed to be unity. Next, assuming that the polyelectrolytes are monodisperse (relatively narrow LPE and BPE fractions were used by Kharenko et al.[46]) and that their true molecular weights are equal to the weight-average values listed in Table 3, we obtained the calculated M_{calc} from the formulae

$$M_{calc} = \bar{P}_{LPE}\bar{M}_{un}, \qquad (2)$$

where $\bar{M}_{un}$ is the average molecular weight of a unit of the N-PEC species, and

$$\bar{M}_{un} = \bar{M}_{(LPE)} + \varphi(M_{(BPE)} - M), \qquad (3)$$

where M is the molecular weight of the low-molecular-weight salt liberated on dissolution as a result of reaction (I). Table 3 shows that the measured values of $\bar{M}_w$ agree satisfactorily with those calculated by Eqns.(2) and (3), which convincingly demonstrate that the composition of each species of the N-PEC investigated does indeed incorporate in this instance a single LPE macromolecule and the corresponding number of BPE macromolecules ($\bar{n}_{BPE}$):

$$\bar{n}_{BPE} = \varphi(\bar{P}_{LPE}/\bar{P}_{BPE}). \qquad (4)$$

It will be shown below that the maintenance of specific conditions is necessary for the formation of such unassociated N-PEC. The results presented in Table 3 again confirm the conclusion that the N-PEC can be regarded as individual macromolecular compounds characterised by their specific molecular weights. It is seen from a comparison of the radii of inertia $(\bar{R}_g^2)^{1/2}$ for the N-PEC and the LPE that the dimensions of the N-PEC species are appreciably smaller than those of the charged chains of the corresponding LPE.

Table 3. Characteristics of the individual polyelectrolytes and the N-PEC formed from them and having the composition $\phi = 0.33$.[46]

(N-PEC)	$10^{-5}\bar{M}_w$ (LPE)	$10^{-5}\bar{M}_w$ (BPE)	pH	I, M	$10^{-5}\bar{M}_w$ N-PEC expt.	$10^{-5}\bar{M}_w$ N-PEC calc.	$(\bar{R}_g^2)^{1/2}$, Å	$10^4 A_2$
PDMAEMA.HCl-PP	6.3	0.17	4.0	0.100	6.7	6.8	350 (520)	2.9 (8.2)
PDMAEMA.HCl-PAA	5.3	0.14	5.0	0.100	5.6	5.6	435 (485)	8.6 (9.4)
PP-Na-5,6-ionene	0.66	0.14	7.0	0.025	0.66	0.85	—	17 (143)

Remarks: The values in brackets refer to the LPE in the LPE–BPE systems.

It is also seen that the formation of the N-PEC is accompanied by a decrease of the second virial coefficient of the solution A_2. The causes of these changes will be examined below. Here we shall only note that the relative changes in the above parameters on formation of the N-PEC are not the same for different pairs of polyelectrolytes even if the polyelectrolyte complexes have the same composition expressed in terms of ϕ. It may be that this is associated with the characteristics of the structures of the initial polyelectrolyte, in particular, with the disposition of the ionogenic groups relative to the main chain and also with the ratio of the hydrophilic and hydrophobic groups in the units of the interacting polyelectrolyte components. The degree of the mutual steric correspondence of the polyions forming the N-PEC can apparently also play a definite role. These questions have not as yet been adequately investigated.

We shall now consider how the macromolecular parameters of the N-PEC in aqueous solution behave as a function of ϕ. Table 4 presents the results of a light-scattering study of N-PEC solutions obtained in the PDMAEMA.HCl—PP-Na system. Evidently, when the composition of the polyelectrolyte complexes ϕ is varied within a fairly wide range (from 0.5 to 0.067), their weight-average molecular weight hardly changes and is identical, within the limits of the error of the measurements, with the values calculated from Eqns.(2) and (3). Over the entire range of compositions, each PEC species contains a single LPE chain. The average number of BPE chains in each species, calculated from Eqn.(4), decreases from 10 to 1. Thus each N-PEC species, under conditions where it contains only one LPE chain, can be reasonably regarded as a kind of individual complex macromolecule whose composition with respect to the polyelectrolyte components can be readily varied within certain limits having specified their initial ratio Z. Clearly the constancy of the experimental molecular weights and the

slight variation of the calculated molecular weights, under the conditions of a 10-fold decrease of the population of the LPE chains by BPE chains is due to the compensation effect caused by the liberation of counterions into the solution as a result of the formation of the PEC.

Table 4. The influence of the composition of the N-PEC in the PDMAEMA.HCl ($\bar{M}_w$ = 6.3 × 10^{-5})–PP-Na ($\bar{M}_w$ = 1.7 × 10^{-4}) system on its molecular characteristics (pH 4.0 in 0.1 M NaCl at 20 °C).[46]

φ	$\partial n/\partial c$, dl g^{-1}	$10^{-5}\bar{M}_w$ (N-PEC)		$\bar{n}_{BPE}$	$(\overline{R_g^2})^{1/2}_z$, Å	$10^4 \cdot A_2$	S
		expt.	calc.				
0	0.161	6.3	—	—	510	8.2	2.5
0.07	0.158	7.15	6.4	1.4	480	6.5	2.7
0.10	0.158	6.9	6.4	2.0	440	5.9	2.8
0.13	0.158	7.35	6.5	2.3	430	5.2	—
0.20	0.158	6.75	6.6	3.9	400	4.9	3.7
0.33	0.154	6.7	6.8	6.5	350	2.9	6.0
0.50	0.156	7.0	7.0	10	270	1.1	5.9

Notation: $\bar{n}_{BPE}$ = average number of macromolecules in the N-PEC species ($\bar{n}_{LPE}$ = 1); S = sedimentation coefficient (in Svedberg units) determined for [N-PEC] = [PDMAEMA.HCl] = 0.35 wt.%.

The mean square radius of inertia $(\overline{R_g^2})^{1/2}$ of the N-PEC is more sensitive to changes in composition than the molecular weight. In particular, $(\overline{R_g^2})^{1/2}$ of a complex macromolecule having the composition ϕ = 0.5 is almost a factor of two smaller than the $(\overline{R_g^2})^{1/2}$ of the macromolecule of the free LPE (Table 4). The dependence of $(\overline{R_g^2})^{1/2}$ of the N-PEC macromolecules on ϕ, based on the data in Table 4, is illustrated in Fig.8*a*. Evidently their average size decreases monotonically with decrease of the population of the LPE chains by the BPE chains, approaching the average size of the statistical coil of the free LPE in the same solvent. The results on the measurement of the radius of inertia of the N-PEC macromolecule as a function of composition are important for the justification of the general scheme for the structure of the N-PEC species assuming the existence of sufficiently long two-stranded ladder sections. This scheme was assumed above *a priori* on the basis of indirect data concerning the structure of the S-PEC in the solid phase already mentioned. It can now be shown that the adopted fundamental motif of the ladder-like relative distribution of the chains constituting the PEC has in fact no alternative.

Indeed Table 4 shows that the values of $(\overline{R_g^2})^{1/2}$ for the N-PEC macromolecules with composition ϕ = 0.067 and for the statistical coil of the free LPE differ by only 5–6%. At the same time, on average each 15th unit of the LPE chain of the N-PEC species having the composition ϕ = 0.067 is involved in the formation of a salt linkage with a unit of the BPE chain: for $\theta \cong 1$, each LPE chain with a length equivalent to ~3000 units is linked to a BPE chain with a length equivalent to ~170 units. If it is assumed that the two chains are randomly intertwined, then, on passing from the free LPE to the N-PEC, one would have to expect a much greater relative decrease of the radius of inertia, which follows, for example, from calculations by the Monte Carlo method of the change in the average dimensions of a model chain on random formation of irreversible intramolecular cross-links[49]. In particular, it has been shown that, even for a Gaussian chain comprising 100 segments and existing under θ-conditions, the relative decrease of the radius of inertia accompanying the formation of on average five fixed cross-links should be ~35%. Naturally, in the case of the N-PEC one is dealing with the formation of reversible salt linkages within its species. However, if the statistical weight of the randomly formed cross-links in the N-PEC structure had been considerable, the experimentally observed relative change in the average dimensions of the macromolecular coil on passing from the free LPE to the N-PEC would have been significantly greater.

Consequently, in the water-soluble N-PEC form the contour line of the fragment of the LPE chain is close to the contour line of the BPE chain interacting with it. In other

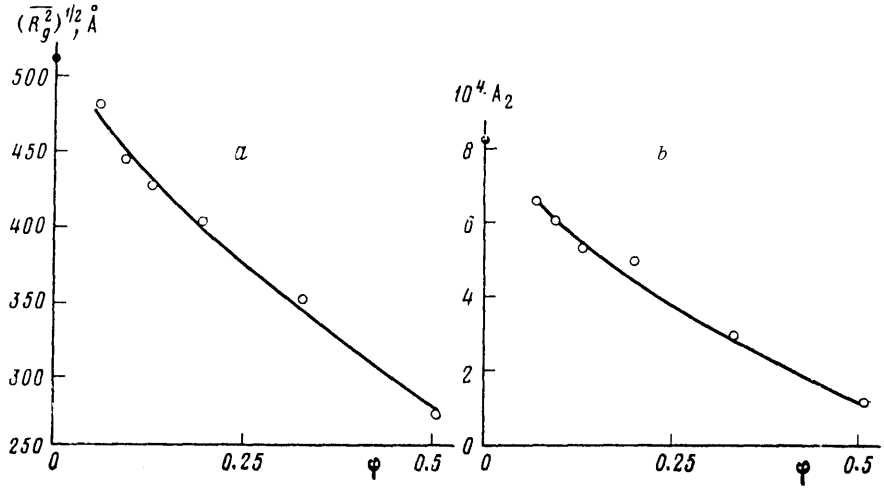
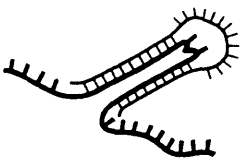


Figure 8. Dependence of the particle size $(\overline{R_g^2})^{1/2}$ (*a*) and of the second virial coefficient A_2 (*b*) for solutions of the PDMAEMA.HCl–PP N-PEC on the composition of the N-PEC (ϕ); for conditions, see caption to Fig.7.[46]

words, a structure in which both interacting chains are in the main distributed parallel to one another in all probability predominates in the N-PEC. At the same time, in the course of thermal movement, the BPE chains can in general migrate from one LPE section to another and different N-PEC macromolecules in solution can even exchange their constituent polyelectrolyte components†.

The two-stranded sections of the PEC species do not necessarily have the form of extended rods. On the other hand, by virtue of their increased hydrophobic properties, they should tend to fold at the sites of the "intraladder" loop-shaped defects already mentioned, forming drop-like clusters, as shown in Scheme *E*.

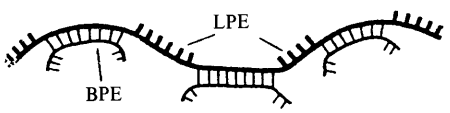
Scheme *E*



The conformation of the complex macromolecule of the water-soluble N-PEC illustrated in this Scheme appears probable also from general thermodynamic considerations. Conformations of this type for fixed values of ϕ and θ apparently correspond to the minimum free energy (maximum entropy), since they contain long sections of free LPE. By virtue of the reversibility of the formation reaction of the N-PEC, the system can "find" the optimum set of conformations by the method of "trial and error".

With increase of ϕ, i.e. with increase of the number of BPE chains incorporated in the N-PEC molecule, the number of two-stranded ladder sections in this molecule naturally also increases, as shown in Scheme *F*.

Scheme *F*

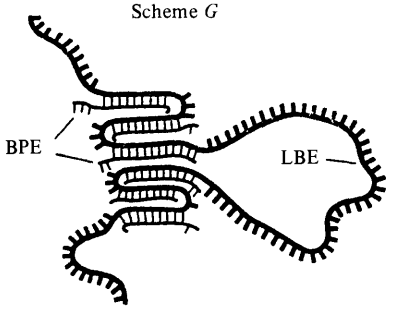


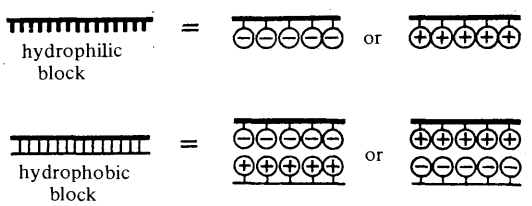
Each section of this kind constitutes a set of cooperatively interacting oppositely charged chain units. It exhibits an enhanced rigidity and relatively weak hydrophilic properties (i.e. relatively pronounced hydrophobic properties). This is why the N-PEC "overloaded" with the BPE for $\phi > \phi_{char}$ lose their solubility in water. The S-PEC are insoluble in water for the same reason. On the other hand, the BPE-free LPE sections in the N-PEC macromolecule are relatively flexible and hydrophilic. Consequently the N-PEC molecule can be regarded as a linear sequence of fairly long hydrophobic and hydrophilic blocks. In other words, the N-PEC constitutes a kind of block-copolymer. The hydrophilic blocks are carriers of properties typical for the usual linear polyelectrolytes. Water behaves as a good solvent in relation to one-stranded polyelectrolyte sequences and as a poor solvent in relation to two-stranded hydrophobic sequences. Consequently the hydrophobic blocks of the N-PEC macromolecules in an aqueous solution should collect together, i.e. should become segregated as a result of non-polar interactions.

†The question of the intramolecular and intermolecular dynamics of the PEC is of considerable interest and merits special study. Some primary information about this problem can be found in Kabanov's paper[21].

In fairly dilute solutions such segregation is intramolecular, which happens, in particular, in the systems presented in Table 4. The progressive decrease of the average dimensions, i.e. of the quantity $(\overline{R}_g^2)^{1/2}$, for complex N-PEC macromolecules as they become enriched in the BPE chains can serve as a quantitative measure of the intramolecular segregation. Scheme *G*, below, illustrates the intramolecular segregation of the hydrophobic blocks in water-soluble N-PEC,

Scheme *G*





A change in the composition of complex N-PEC macromolecules is also accompanied by a change in the thermodynamic characteristics of their solutions. It follows from Table 4 that the second virial coefficient of the solution A_2 increases with decrease of ϕ, i.e. with decrease of the fraction of LPE units incorporated in the hydrophobic blocks. With decrease of ϕ, the quantity A_2 tends to the value characteristic of the solution of the free LPE (Fig. 8*b*). The latter shows that the electrostatic repulsion between LPE units having like charges and forming one-stranded hydrophilic blocks makes the main contribution to the formation of the excluded volume in complex N-PEC macromolecules. According to the Donnan–Guggenheim theory[50], the contribution of the electrostatic repulsion of the polyion units to the overall second virial coefficient can be expressed as follows:

$$A_{2el} = 10^3 z^2/4M^2 I \ , \qquad (5)$$

where z is the effective charge of the polyion, M its molecular weight, and I the concentration of the low-molecular-weight (1:1) electrolyte. An important property of the parameter $A_{2,el}$ of an ordinary polyelectrolyte is its proportionality to the square of the degree of ionisation of the corresponding polyion. Evidently, for the N-PEC considered, this parameter can be varied within wide limits by altering the composition of the complex macromolecule ϕ. The effective charge on the N-PEC macromolecules in the pH range corresponding to the complete ionisation of the LPE units depends on the composition ϕ in the following manner:

$$z/M = \gamma(1-\varphi)/M_0 \ , \qquad (6)$$

where M_0 is the mass of the unit of the polyion and γ the degree of binding of the low-molecular-weight counterions. Thus the parameter $A_{2,el}$ should be proportional to the quantity $(1-\phi)^2$ for a solution of N-PEC block macromolecules, in which the hydrophobic ladder blocks are combined into a system of compact intramolecular clusters and the

charged hydrophilic blocks are on the periphery of the species and are responsible for the solubility of the N-PEC. The dependence of A_2 on $(1 - \phi)^2$ is plotted in Fig.9 on the basis of the data in Table 4. It is evidently linear. The parameter A_2 tends to the value for the solution of the free LPE as ϕ diminishes. For $\phi \to \phi_{char} = 0.56$, the quantity A_2 tends to zero. The data presented convincingly confirm the applicability of Scheme *G* to the description of the behaviour of water-soluble N-PEC.

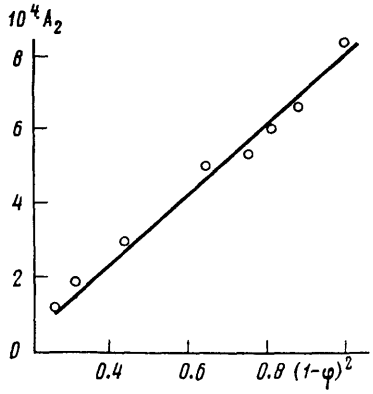


Figure 9. Dependence of the second virial coefficient A_2 for solutions of the PDMAEMA.HCl–PP N-PEC on $(1 - \phi)^2$; for conditions, see caption to Fig.7.[47]

Table 5. The influence of the composition of the PDMAEMA.HCl ($\bar{M}_w = 6.3 \times 10^5$)–PA-Na ($\bar{M}_w = 1.4 \times 10^4$) N-PEC on its molecular characteristics (pH 4.5 in 0.1 M NaCl at 20 °C).[46]

φ	$10^{-5}\bar{M}_w$ (N-PEC)		$\bar{n}_{BPE}$	$(\bar{R}_g^2)^{1/2}$, Å	$10^4 \cdot A_2$	S
	expt.	calc.				
0	5.3	—	—	485	9.4	2.0
0.125	5.5	5.4	2.1	475	9.5	2.1
0.20	6.0	5.5	3.4	460	9.0	2.3
0.33	5.6	5.6	5.6	435	8.6	2.6
0.50	5.6	5.8	8.5	400	7.6	3.3

Notation: see Table 4.

The dependence of the sedimentation coefficient S on the composition of the N-PEC macromolecule for a fixed concentration of the solutions is also in good agreement with the ideas developed above (Table 4). The coefficient S steadily decreases with decrease of ϕ, approaching the value of S for the solution of free LPE. It is evident that, since the molecular weight of the N-PEC depends little on its composition ϕ, the main factor determining the behaviour of S is the average size of the sedimenting particles, which increases with decrease of ϕ as a consequence of the increased degree of swelling of the particles caused by the mutual electrostatic repulsion of the excess positively charged LPE units in the complex macromolecules.

Scheme *G*, describing the structure of the water-soluble N-PEC, is fairly general. It is apparently valid for a wide range of N-PEC with different chemical compositions, provided that they are products of completed interpolymer reactions, i.e. for $\theta \cong 1$. Tables 5 and 6 present the characteristics of two other varieties of the water-soluble N-PEC measured by the light-scattering and high-speed sedimentation methods. The dependences of $(\bar{R}_g^2)^{1/2}$, A_2, and S on ϕ obtained are also fully consistent with the ideas described above.

Table 6. The influence of the composition of water-soluble N-PEC formed from PP-Na ($\bar{M}_w = 6.6 \times 10^4$) and 5,6-ionene bromide ($M_w = 1.4 \times 10^4$) on their molecular characteristics (pH 7.0 in 0.025 M NaBr at 20 °C).[46]

φ	$10^{-4}\bar{M}_w$ (N-PEC)		$\bar{n}_{BPE}$	$10^3 \cdot A_2$	S
	expt.	calc.			
0	6.6	—	—	14.3	2.2
0.125	6.4	7.3	1.2	4.8	2.5
0.20	6.2	7.8	1.9	2.2	2.7
0.33	6.6	8.5	3.1	1.7	3.4

Notation; see Table 4.

The next important problem is that of the influence of the molecular weights of the LPE and the BPE on the macromolecular characteristics of the water-soluble N-PEC. Table 7 presents the values of $\bar{M}_w$, $(\bar{R}_g^2)^{1/2}$, and A_2 measured by the light-scattering method for the PDMAEMA.HCl–PP-Na N-PEC having the constant composition $\phi = 0.33$. The condition $\bar{P}_{LPE}/\bar{P}_{BPE} \gg 1$ holds for the entire series of systems. The systems differ from one another only by the molecular weights of the initial polyelectrolyte components. Table 7 shows that, when the ratio $\bar{P}_{LPE}/\bar{P}_{BPE}$ is varied within wide limits (from 5 to 20) by varying the values of both $\bar{P}_{LPE}$ and $\bar{P}_{BPE}$, only one LPE macromolecule is incorporated in the N-PEC species. In other words, in this case too the N-PEC species can be regarded as individual complex macromolecules in the dilute solution at fixed concentrations of the components and ionic strengths over the entire experimental range of molecular weights.

Table 7. The influence of the molecular weights of the LPE and the BPE on the molecular characteristics of the PDMAEMA.HCl–PP-Na N-PEC ($\phi = 0.33$; pH 4.0 in 0.1 M NaCl at 20 °C).[46]

$10^{-5}\bar{M}_w$ (PDMAEMA.HCl)	$10^{-4}\bar{M}_w$ (PP-Na)	$\bar{P}_1/\bar{P}_2$	$10^{-5}\bar{M}_w$ (N-PEC)	$\bar{n}$	$(\bar{R}_g^2)^{1/2}$, Å	$10^4 \cdot A_2$
1.64	1.7	5.1	1.9	1.7	—	2.9
6.3	1.7	19.5	6.7	6.4	350	2.9
6.3	5.7	5.8	7.3	1.9	380	2.7
6.3	6.6	5.0	7.2	1.5	370	2.8

Notation: $\bar{n}$ is the average number of macromolecules in the N-PEC species; the values for PP are indicated, those for PDMAEMA.HCl being unity.

It is significant that the average dimensions of the N-PEC macromolecules and the second virial coefficients of their solutions with the specified values of $\bar{P}_{LPE}$ and ϕ are almost independent of $\bar{P}_{BPE}$. This agrees with ideas concerning

the structure of the complex macromolecules summarised in Scheme *G*. The segregation of the hydrophobic block in these macromolecules is again intramolecular. However, in other cases the change in the hydrophilic–hydrophobic balance in the N-PEC macromolecules with increase of ϕ and hence of the number of hydrophobic blocks can naturally lead also to their intermolecular segregation, i.e. to the formation of N-PEC species containing more than one LPE chain. Such species must be regarded as associated and consisting of individual N-PEC macromolecules.

At the beginning of this Section (Table 4) it was shown, in particular, that solutions of the N-PEC obtained from PDMAEMA.HCl and PP-Na with the composition $\phi \leqslant 0.5$ contain individual complex PEC macromolecules under the chosen conditions. However, when a comparatively small additional amount of the BPE, which is insufficient to cause phase separation in the system, is added to such a solution, the situation changes sharply. This is expressed primarily by a change in the Zimm diagram which assumes a form characteristic of solutions containing associated macromolecules (Fig.10). The double extrapolation plot shows that such associated species are entirely stable on dilution. The N-PEC species with the composition $\phi = 0.56$ has $\bar{M}_w = 2.8 \times 10^6$ according to light scattering data, which exceeds by a factor of four the $\bar{M}_w$ for the individual complex macromolecule with the composition $\phi = 0.5$. Consequently each such N-PEC species actually consists on average of four N-PEC macromolecules with the same composition ϕ.

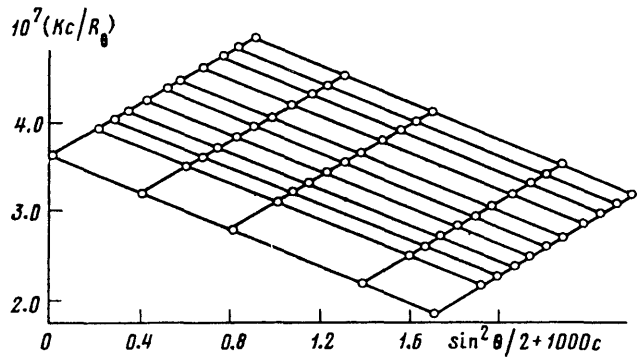
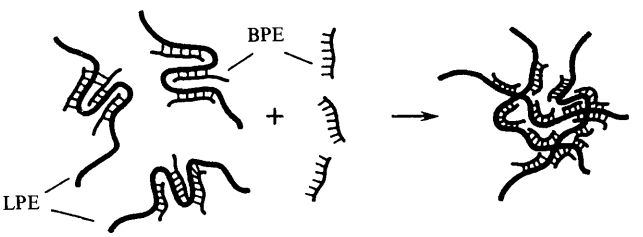


Figure 10. Zimm diagram for a solution of the PDMAEMA. .HCl–PP N-PEC having the composition $\phi = 0.56$ at pH 4.0 in 0.01 M NaCl at 20 °C; for the values of $\bar{M}_w$, see Fig.7.[52]

The association phenomena can be represented by Scheme *H*.

Scheme *H*



The formation of the associated species is accompanied by a sharp decrease of the second virial coefficient A_2 and its becoming negative ($A_2 = -4.5 \times 10^{-5}$). The species comprising associated N-PEC macromolecules with $\phi = 0.56$ is extremely compact and its average size $[(\bar{R}_g^2)^{1/2} = 270$ Å] is virtually identical with the average size of the N-PEC macromolecule of similar composition ($\phi = 0.5$). The behaviour described is characteristic of soluble N-PEC, which do not exhibit a great tendency towards association and give rise to associated species only in the vicinity of characteristic compositions defining their solubility limit. The association phenomena in solutions of such N-PEC resemble the pre-critical phenomena in solutions of ordinary high-molecular-weight compounds, which occur within narrow ranges of conditions near the phase separation points[51].

However, there exists an extensive group of soluble N-PEC which tend to form associated species over an extremely wide range of compositions[52]. In particular, such N-PEC include polyelectrolyte complexes formed by PA-Na and ionenes, for example, by PA-Na and 5,6-ionene bromide. Table 8 presents the characteristics of these N-PEC with the constant composition $\phi = 0.33$, which are formed by PA-Na fractions of different molecular weights. Knowing the molecular weights of the initial polyelectrolyte components and the N-PEC species, the average number of the LPE and BPE chains incorporated in the N-PEC species can be calculated with the aid of the procedures described above. Table 8 shows that, regardless of the molecular weight of the LPE, which was varied by more than an order of magnitude, the N-PEC associated species, formed under the experimental conditions, each incorporate three PA-Na macromolecules. The number of 5,6-ionene macromolecules per associated species corresponds to the composition $\phi = 0.33$ and increases in proportion to the molecular weight of the LPE. The second virial coefficient of the solution then remains virtually constant, while the size of the N-PEC species increases with increase of their mass. This shows that the structure of the species of the polyelectrolyte complex does not undergo qualitative changes with increased length of the LPE chains. Thus each N-PEC species in the systems described can be formally regarded as an associated species formed by three individual complex N-PEC macromolecules. The structure of such an associated species is represented on the right-hand side of Scheme *H*.

Table 8. The influence of the molecular weight of PA-Na (LPE) on the molecular characteristics of the PA-Na–5,6-ionene ($\bar{M}_w = 1.4 \times 10^4$) N-PEC ($\phi = 0.33$; pH 7.2 in 0.025 M NaBr at 20 °C; $n_{LPE} = 3$ [52]).

$10^{-4}\,\bar{M}_w$ (PA-Na)	$10^{-4}\,\bar{M}_w$ (N-PEC)	$\bar{n}$BPE	$(\bar{R}_g^2)^{1/2}$, Å	$10^3 \cdot A_2$
1.4	5.0	2.2	—	2.0
7.5	28	11.3	290	1.8
12	38	18.1	300	1.9
18	69	27.2	400	1.9
41	150	61.7	750	1.9

The phenomena involving the association of complex macromolecules in N-PEC solutions are analogous to the micelle-formation processes in solutions of the usual block-copolymers in selective solvents. The degree of association of the N-PEC for the specified composition ϕ is little sensitive to changes in the molecular weight of the LPE. It is determined primarily by the ratio of the numbers of the LPE units incorporated in the hydrophilic and hydrophobic blocks, i.e. by the composition of the N-PEC. It is known

that the degree of association of the macromolecules of the usual block-copolymer in solutions also depends little on their molecular weights. It is largely determined by the ratio of the lyophobic and lyophilic blocks[53]. The change in the composition of the N-PEC is accompanied in exactly the same manner by a change in the degree of association of their species. This follows from Table 9. It is seen that an increase in the relative content of the LPE units in the N-PEC species, i.e. a decrease of ϕ, leads to a gradual decomposition of the associated species into the individual complex macromolecules.

Table 9. The influence of the composition of the N-PEC on its molecular characteristics[52].

φ	$10^{-5}\bar{M}_w$ (N-PEC)	$\bar{n}$LPE	$\bar{n}$BPE	$10^8 \cdot A^2$
PA-Na ($\bar{M}_w = 1.2 \times 10^5$)–5,6-ionene bromide ($\bar{M}_w = 1.4 \times 10^4$), pH 7.2 in 0.025 M NaBr at 20 °C				
0.07	1.8	1	1.4	11.8
0.10	1.8	1	1.8	10.3
0.13	1.8	1	2.4	7.4
0.20	2.6	2	7.3	3.8
0.33	3.8	3	18.1	1.9
PA-Na ($\bar{M}_w = 2.0 \times 10^5$)–PDMAEMA.HCl ($\bar{M}_w = 7.7 \times 10^4$), pH 8.2 in 0.03 M NaCl at 20 °C				
0.2	2.9	1	1	4.1
0.33	4.8	2	3.4	1.8

The N-PEC formed by high-molecular-weight sodium polymethacrylate (LPE) and PVP-C_2H_5Br (BPE) also exhibit a high tendency towards association[52]; the characteristics of their behaviour are analogous to those considered above.

As shown above, the processes involving the formation and decomposition of the N-PEC associated species can be controlled by altering the composition of the N-PEC. The degree of ionisation of the LPE units incorporated in one-stranded hydrophilic blocks exerts a significant influence on these processes. If the LPE is a weak polyelectrolyte, a decrease in the degree of ionisation is accompanied by a decrease in its lyophilising capacity and leads to a progressive association of the N-PEC macromolecules up to their precipitation from the solution. This is why the N-PEC in which a polycarboxylic acid plays the role of the LPE and which have nearly the characteristic composition are soluble only in alkaline media at pH > 7. Correspondingly the N-PEC incorporating weak polymeric bases as the LPE acquire a capacity for dissolution only in acid media at pH < 7. The degree of association depends also on the degree of binding of the counterions to the free sections of the LPE. Table 10 presents the characteristics, in the presence of 0.025 M NaCl and KCl, of the N-PEC formed from PA-Na and 5,6-ionene bromide ($\phi = 0.33$). Evidently the replacement of the Na^+ counterions by the K^+ counterions, which are less strongly bound to the carboxylate groups of the LPE, entails the decomposition of the N-PEC associated species.

The capacity for association is also determined by the chemical structure of the LPE and BPE constituting the N-PEC. This question has been hardly discussed in the literature partly owing to the insufficiency of rigorous experimental data. Nevertheless, the pairs of polyelectrolytes forming the N-PEC can apparently be divided into two large groups. The subdivision can be based on a comparison of the distances between the neighbouring ionogenic groups in the LPE and BPE chains.

The first group includes pairs for which the neighbouring ionogenic groups in the LPE are separated by larger distances than in the BPE, for example, PDMAEMA.HCl–PA-Na and PDMAEMA.HCl–PP-Na. The amino-groups in PDMAEMA.HCl are far from the main chain and hence from one another. In the PA and PP chains the negatively charged units are closer to one another. Presumably in the corresponding PEC the BPE chain "spreads" over the LPE chains, occupying the section of the latter containing a relatively smaller number of units than in the BPE. Some of the BPE units are then not included in the system of intermolecular salt linkages, i.e. they are, as it were, overlooked. The effective fraction of the units incorporated in the hydrophilic blocks can then prove to be greater than the values calculated on the basis of stoichiometry. In fact, in the case under consideration the hydrophobic blocks should include a smaller number of the LPE units than the BPE units. The reduced tendency of the complex macromolecules towards association for compositions differing from the characteristic compositions ($\phi < \phi_{char}$) may be a consequence of this. Another consequence is the relatively high values of ϕ_{char}, for example, for the N-PEC formed from PDMAEMA.HCl and PA-Na ($\phi_{char} > 0.5$, Table 5).

Table 10. The influence of the nature of the LPE counterion on the molecular characteristics of the PA-Na ($\bar{M}_w = 1.2 \times 10^5$)–5,6-ionene ($\bar{M}_w = 1.4 \times 10^4$) N-PEC ($\phi = 0.33$; pH 8.0; salt concentration 0.025 M; 20 °C).[52]

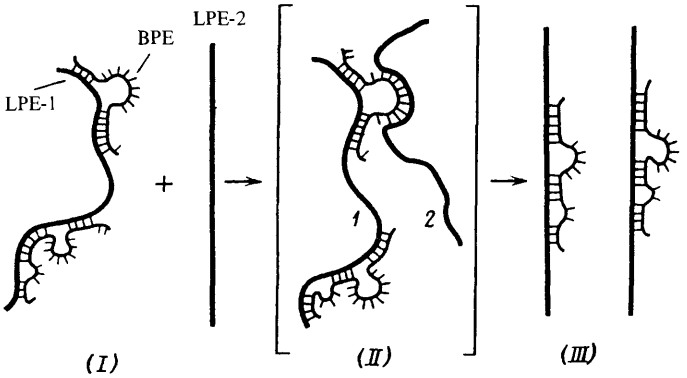
Salt	$10^{-5}\bar{M}_w$ (N-PEC)	$\bar{n}$LPE	$\bar{n}$BPE
NaCl	4.00	3	18.2
KCl	2.25	2	12.1

The second group of the N-PEC includes those for which the opposite condition holds, i.e. the distances between the neighbouring ionogenic groups in the LPE are smaller than in the BPE. Evidently such systems include particularly those which are symmetrical in relation to the systems examined above in which the LPE and BPE have changed places. Table 9 shows that the corresponding N-PEC have smaller values of ϕ_{char}. Presumably the number of units in the LPE section occupied by the BPE chain is greater than $\bar{P}_{BPE}$. The effective fraction of the LPE units incorporated in the hydrophilic blocks then falls, which actually implies a decreased lyophilising capacity of the LPE. A typical example of such a system is the PA-Na–5,6-ionene N-PEC examined in detail previously. The distance between the neighbouring quaternary nitrogen atoms in the BPE chain is much greater than the distance between the neighbouring COO^- groups in the LPE. Accordingly, the complex macromolecules formed by the above pair exhibit an enhanced tendency towards association.

In concluding this Section, we shall consider in broad outline the mechanism of the decomposition of the N-PEC associated species induced by a change in their composition. If the free LPE is added to solutions of the associated N-PEC, a gradual decomposition of the associated species is observed. For a certain ratio of the LPE and the BPE characteristic of each pair of the initial polyelectrolytes, the associated species decompose to the individual N-PEC complex macromolecules. This is illustrated by the data in Table 9.

The decomposition of the N-PEC associated species is accompanied by a redistribution of the BPE chains among a large number of the LPE chains. This leads ultimately to the formation of individual N-PEC species containing one LPE chain. However, their composition is significantly different from that of the initial associated species. The process described naturally presupposes the transfer of the BPE chains from one set of LPE chains to another. It is of interest that such transfer takes place in solutions from which free BPE macromolecules are absent. This is indicated by both light-scattering data and high-speed sedimentation data. Consequently the transfer of BPE takes place via the formation of intermediate macromolecular compounds, which then decompose to form the final products. The transfer can be represented by Scheme *I*.[21]

Scheme *I*



The intermediate polyelectrolyte complex (II) is formed via the addition of units of the free chain 2 to the section of the BPE chain incorporated in a defect of the N-PEC. The compound formed is unstable, since it possesses an increased electrostatic free energy. It therefore decomposes into two new N-PEC species having a different composition. This mechanism of the exchange of the BPE chains by the N-PEC species containing them is apparently fairly general for a wide variety of processes occurring with participation of polyelectrolyte complexes[54].

We emphasise yet again that the soluble N-PEC are macromolecular compounds formed as a result of reversible interpolymer reactions. This is why the reversible nature of the interaction of the macromolecules forming the N-PEC species presupposes the possibility of the interchange of the hydrophilic and hydrophobic blocks within such species and also between different species.

V. THE INFLUENCE OF LOW-MOLECULAR-WEIGHT SALTS ON THE BEHAVIOUR OF POLYELECTROLYTE COMPLEXES IN AQUEOUS SOLUTIONS

Certain properties of aqueous N-PEC solutions were briefly considered in the preceding two sections, mainly in connection with the factors altering the lyophilising capacity of the LPE. In particular, it was found that a decrease in the effective charge on the hydrophobic N-PEC blocks, which can be achieved by altering the pH of the solution or the nature of the LPE counterions, is accompanied by a change in the degree of association of the N-PEC species and ultimately by the loss of the solubility of the N-PEC. Situations were described where the precipitation of the PEC is not accompanied by a change in its composition.

However, the behaviour of the N-PEC in aqueous solutions of low-molecular-weight salts is of greatest interest. In the investigations summarised above mainly uni-univalent electrolytes—alkali metal halides and quaternary ammonium salts—were used[55]. Fig.11 presents as an example the curve for the turbidimetric titration of a solution of the PMA-Na–PVP.C_2H_5Br N-PEC having $\phi = 0.33$ with an NaBr solution. It is possible to distinguish three ranges of variation of the ionic strength of the solution to which regions I, II, and III in Fig.11 correspond.

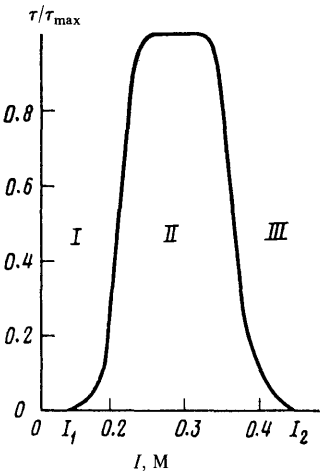


Figure 11. Curves for the turbidimetric titration of a solution of the PMA-Na ($\bar{M}_w = 2.6 \times 10^5$)–PVP.$C_2H_5Br$ ($\bar{M}_w = 6 \times 10^4$) N-PEC having the composition $\phi = 0.33$ with NaBr solution; at pH 7.5 and 20 °C.[55]

In region I an increase in the salt concentration in solution is not accompanied by a change in the phase state of the system—the latter remains homogeneous. After the attainment of a certain ionic strength I_1, the system begins to turn turbid and a further increase of the ionic strength is accompanied by a progressive increase of turbidity. In region II the system is of the heterophase type. A fairly broad range of variation of the salt concentration corresponds to this region. The right-hand boundary of region II is characterised by a decrease of turbidity. Finally, at an ionic strength of the solution $I = I_2$, the system again becomes homogeneous. Region III corresponds to ionic strengths $I > I_2$; here the system remains homogeneous.

The behaviour described is characteristic of all the N-PEC investigated at the present time. It can be illustrated in relation to examples of associated N-PEC, in particular PA-Na–5,6-ionene and PA-Na–PDMAEMA as well as non-associated N-PEC such as PDMAEMA.HCl–PP and PDMAEMA.HCl–PAA. However, one should note that the positions of the boundaries between regions I, II, and III, i.e. the values of I_1 and I_2, depend markedly on the nature of the polyelectrolytes forming the N-PEC and also on the nature of the low-molecular-weight salts inducing the transformations considered.

We shall follow in succession the changes in the state of the PEC in the above three regions corresponding to the variation of the ionic strength of the solution. For this purpose, we shall return to the PMA-Na–PVP.C_2H_5Br system. Fig.12

presents the results of the study by the light-scattering method of the corresponding aqueous salt solutions in region I (cf.Fig.11). It is seen that an increase in the ionic strength of the solution (an increase of the NaBr concentration) is not accompanied by a change in the molecular weights of the N-PEC associated species (curve *1*). In the range of ionic strengths indicated each associated species retains the composition $\phi = 0.33$ and each contains on average three LPE (PMA-Na) chains. The sedimentation diagrams for the solutions contain a single peak (see Fig.16 below). Thus, for $I < I_1$, the N-PEC investigated behaves like an individual macromolecular compound. On the other hand, an increase in the ionic strength of the solution in region I leads to a considerable decrease in $(\overline{R}_g^2)^{1/2}$, i.e. to a decreased average particle size (curve *2*). The second virial coefficient then also decreases and, as the boundary between regions I and II, i.e. the point $I = I_1$, is approached, it tends to zero, which indicates an impairment of the thermodynamic properties of the solvent.

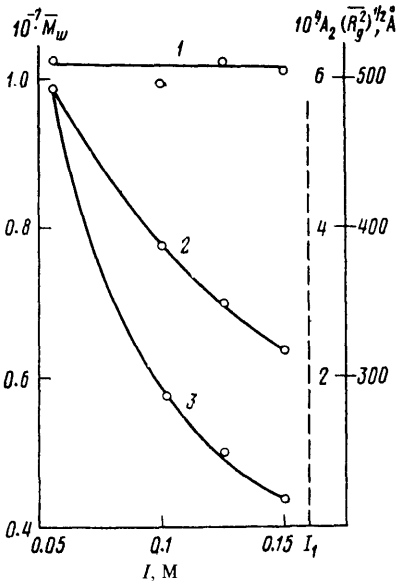


Figure 12. Molecular characteristics of the PMA-Na–PVP.C_2H_5Br N-PEC having the composition $\phi = 0.33$ as a function of the NaBr concentration in solution: *1*) $\overline{M}_w$ (N-PEC); *2*) $(\overline{R}_g^2)^{1/2}$; *3*) A_2; for conditions, see caption to Fig.11.[55].

Solutions of the unassociated N-PEC, an example of which may be provided by the PDMAEMA.HCl–PAA and PDMAEMA.HCl–PP systems, also behave analogously in region I. Such behaviour is typical for solutions of the usual flexible-chain polyelectrolytes. It is a consequence of the shielding of sections of the macromolecule by the counterions and of the decrease of the electrostatic repulsion between the LPE units with like charges incorporated in one-stranded hydrophilic blocks. The dependence of the second virial coefficients A_2 of solutions of different N-PEC on the reciprocal of the ionic strength is linear (Fig.13), which is also typical for the usual linear polyelectrolytes [see Eqn.(5)]. Thus the behaviour of the N-PEC in aqueous solutions containing comparatively low concentrations of low-molecular-weight salts is determined mainly by the properties of the charged one-stranded LPE blocks.

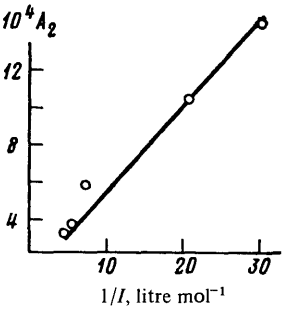


Figure 13. Dependence of the second virial coefficient A_2 for the PDMAEMA.HCl ($\overline{M}_w = 6.3 \times 10^5$)–PP ($\overline{M}_w = 1.7 \times 10^4$) N-PEC solution having the composition $\phi = 0.33$ on the reciprocal of the ionic strength of the solution $1/I$ (NaCl, pH 4.0 at 20 °C).[47]

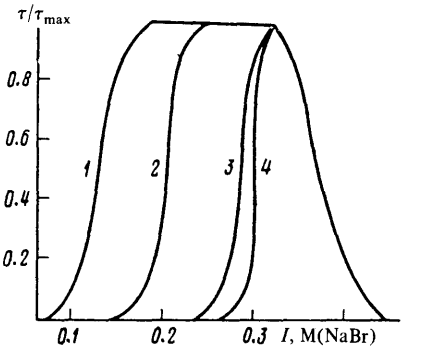


Figure 14. Curves for the turbidimetric titration of solutions of the PMA-Na ($\overline{M}_w = 2.6 \times 10^5$)–PVP.$C_2H_5Br$ ($\overline{M}_w = 6 \times 10^4$) N-PEC having different compositions ϕ [*1*) 0.4; *2*) 0.33; *3*) 0.25; *4*) 0.2] with an NaBr solution at pH 7.5 and 20 °C.[55]

The position of the boundary between regions I and II, i.e. the value of I_1, depends greatly on the composition ϕ of the N-PEC. This is shown in Fig.14 in relation to the PMA-Na–PVP.C_2H_5Br N-PEC. Evidently, with increase of the BPE content in the polyelectrolyte complex species. i.e. with decrease of the fraction of the free LPE units, the boundary between regions I and II shifts towards lower ionic strengths of the solutions. This is also true of the PDMAEMA.HCl–PP and PA-Na–5,6-ionene systems. However, for fairly low values of ϕ, the majority of the N-PEC investigated remain soluble over the entire range of ionic strengths (for $\phi < 0.15$). This result is natural, since a decrease of ϕ implies an increase of the relative content of the hydrophilic blocks made up of ionised LPE units. The ionic strength I_1 also depends on the chemical nature of the low-molecular-weight salt, more precisely on the nature of the LPE counterions.

Fig. 15 presents curves for the turbidimetric titration of the PA-Na–5,6-ionene N-PEC having a fixed composition by various salts. In the series of selected counterions, the ionic strength I_1 varies as follows: $Li^+ < Na^+ < K^+ < TMA^+$ (TMA^+ is the tetramethylammonium ion), i.e. increases with decrease in the constant for the binding of the counterions to the polymeric carboxylic acids[56]. At the same time, I_1 is independent of the nature of the low-molecular-weight LPE ion, whose charge has the same sign as that of the ionised LPE units. Evidently curves *2'*, *2''*, and *2'''*, which refer to cases where an increase of the ionic strength is attained by the addition of the corresponding sodium fluoride, chloride, and bromide, coincide. All the facts presented show that in region I the behaviour of the N-PEC is indeed mainly determined by the properties of the free LPE units. The position of the boundary between regions I and II depends strongly, other conditions being equal, on the chemical nature of the LPE and BPE constituting the complex[5]. However, the available experimental data are as yet insufficient to trace any consistent relations.

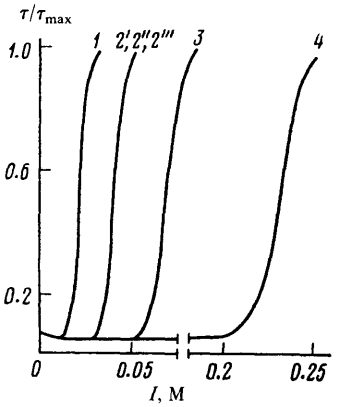


Figure 15. Curve for the turbidimetric titration of solutions of the PA-Na ($\bar{M}_w = 1.8 \times 10^5$)–5,6-ionene ($\bar{M}_w = 1.4 \times 10^4$) N-PEC having the composition $\phi = 0.33$ with solutions of LiCl (curve *1*), NaX [X: *2'*) F^-; *2''*) Cl^-; *2'''*) Br^-], KCl (curve *3*), and $(CH_3)_4NCl$ (curve *4*). Concentration of the N-PEC solution 0.01 wt.% at pH 8.5 and 20 °C.[55]

In region II ($I_1 < I < I_2$) the systems investigated are of the heterophase type for not unduly low values of ϕ. The soluble N-PEC must therefore be synthesised at ionic strengths of the solutions, not exceeding I_1. The behaviour of the PEC in region II differs significantly from the behaviour of the usual individual polyelectrolytes in aqueous salt media, for example, on salting-out. This is manifested primarily by a sharp difference between the compositions of the polymeric products in the coexisting phases. Table 11 presents the results of the analysis of the compositions of the dilute phase for the PDMAEMA.HCl–PP-Na system and the calculated compositions of the concentrated phase, i.e. the precipitate. It is found that, regardless of the composition of the initial system Z, for $\bar{P}_{LPE} \gg \bar{P}_{BPE}$, the S-PEC deposit coexists with a solution of complex macromolecules having the composition $\phi = 0.12–0.14$ (Table 11). For this composition, the N-PEC remains soluble over the entire range of ionic strengths. In the case where $\bar{P}_{LPE} \cong \bar{P}_{BPE}$ the S-PEC deposit coexists with a solution of free LPE (Table 11). Accordingly, the position of the turbidimetric titration curves for solutions of the N-PEC formed by electrostatically complementary polyelectrolytes with similar degrees of polymerisation is independent of the composition Z of the initial system.

Table 11. The composition of the phases coexisting in region II for the PDMAEMA.HCl ($\bar{P}_1 = 3200$)–PP-Na system at pH 4.0 at 20 °C.[55]

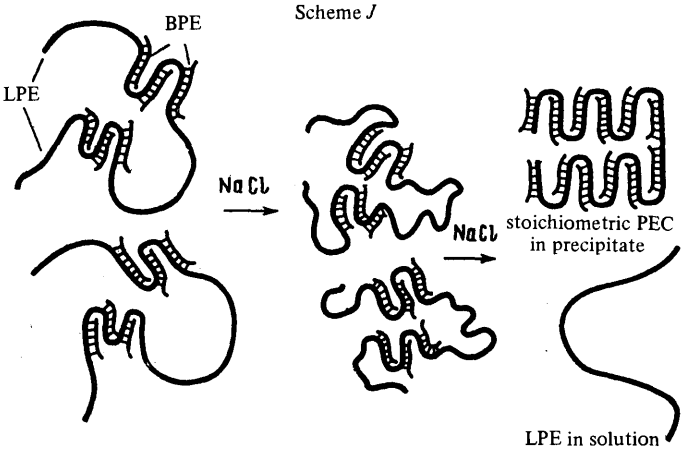
Z	$10^3 \cdot c_1$	$10^3 \cdot c_1'$	$10^3 \cdot c_2'$	φ
		$\bar{P}_2 = 170$; 0.57 M NaCl		
0.17	15.0	11.0	1.5	0.14
0.20	17.5	14.2	1.7	0.12
0.22	20.0	17.1	2.2	0.13
0.25	22.5	20.1	2.5	0.12
0.29	25.0	22.8	2.9	0.13
0.33	30.0	28.5	3.8	0.13
		$\bar{P}_2 = 3000$; 0.85 M NaCl		
0.2	10	4.8	traces	*
0.25	15	9.8	»	*
0.33	20	15	»	*
0.5	25	20	»	*

Notation: c_1 and c_1' are the PDMAEMA.HCl concentrations in the initial mixture and in the supernatant and c_2 and c_2' are the respective concentrations of PP-Na (in basic M) ($c_2 = 5.0 \times 10^{-3}$ basic M); ϕ is the composition of the PEC in solution; in the precipitate $\phi = 1$.

*Free PDMAEMA.HCl.

Thus, on passing from region I to region II, a distinct disproportionation phenomenon is observed, i.e. an inhomogeneous distribution of the BPE chains between the LPE chains. Disproportionation phenomena in interpolymer reactions are known[57]. In the cases considered here the disproportionation is due to the insolubility of the S-PEC. The transition from the uniform to the non-uniform population of the LPE chains by the BPE chains can be represented by Scheme *J*.

Scheme *J*



Evidently the entropy of the two-phase system where S-PEC is present in the concentrated phase (i.e. in the deposit), while in the dilute phase (i.e. in the solution) the N-PEC is depleted in the BPE or simply the free LPE is present, is

higher than the entropy of the system containing the N-PEC precipitate. For a constant total number of interpolymer salt linkages, a minimum in the free energy of the system should correspond to the first state.

The mechanism of the rearrangement of the N-PEC in aqueous salt media in region II is still not entirely clear. Presumably there are at least two pathways leading to disproportionation. One of these presupposes the preliminary salting-out of the N-PEC and its subsequent rearrangement in the concentrated phase with formation of the S-PEC and the liberation of the excess LPE into the solution. Another possible pathway consists in the formation of the S-PEC still in the solution as a result of the chemical reaction involving the transfer of BPE chains from one set of N-PEC species to another with subsequent precipitation of the S-PEC. In the case of associated N-PEC, the latter process can occur within the limits of each individual initial species. None of the postulated pathways excludes the other when applied to the given system—they can occur simultaneously. However, it must be emphasised that the characteristics of the behaviour of the N-PEC in region II are determined by the occurrence of two coupled processes: the physical process of phase separation and the chemical reaction involving the rearrangement of the PEC species.

The state of the species of the polyelectrolyte complex in region II varies with the ionic strength. An increase in the salt concentration is accompanied by the rupture of some of the interchain salt linkages as a consequence of ion exchange, i.e. as a consequence of the replacement of the "LPE unit–BPE unit" bond by two "chain unit–counterion" bonds[34]. For us, it is important that in region II the extent of the ion exchange is not sufficient for the dissociation of the PEC species into individual polyelectrolyte components. This is indicated particularly by the presence of the S-PEC deposit in the system.

Finally we shall consider the transition from the heterogeneous region II to the homogeneous region III. We may note in the first place that the position of the boundary between these regions, i.e. the value of I_2, depends little on the composition Z of the mixture of polyelectrolytes, in contrast to I_1 (Fig.14). The latter can be understood by taking into account the fact that, on passing from region II to region III and further, an increase in the ionic strength entails a far-reaching decomposition of the PEC. In fact I_2 is determined by the initial conditions for the separation of the polyelectrolyte components in the S-PEC, whose composition is naturally constant and independent of the initial ratio of the BPE and the LPE. In region III the fraction of the units θ linked by salt bonds greatly diminishes. There is a corresponding increase of the fraction of disconnected units. For the critical value of θ characteristic of each pair of polyelectrolytes, a sufficient number of hydrophilic sequences, i.e. loops incorporating disconnected units (see Scheme *A*), have accumulated in the S-PEC species. The precipitate then dissolves. The dissolution does not necessarily imply a complete separation of the electrostatically complementary chains in space. They can still be retained near one another by a relatively small number of salt linkages. However, with increase in the ionic strength in region III this number continuously falls. Finally, after the attainment of a sufficiently high concentration of low-molecular-weight salt, the polyelectrolyte complex dissociates completely into the individual polyelectrolyte components.

Fig.16 presents the sedimentation diagrams for the PMA-Na–PVP.C_2H_5Br N-PEC with the composition $\phi = 0.14$ in aqueous salt media. The polyelectrolyte complex having this composition is soluble over the entire range of experimental ionic strengths, i.e. the system is homogeneous at all the ionic strengths investigated. The characteristics of the behaviour of the N-PEC in the vicinity of the boundary between regions II and III and in region III are therefore particularly clearly manifested in relation to this system. Evidently, in the homogeneous system up to the ionic strength $I = 0.4$ M, the N-PEC species sediment with a single peak, i.e. they retain their individuality (curves *1* and *2*). However, on further increase in the concentration of the low-molecular-weight salt, the N-PEC dissociates into the free LPE and BPE. This is indicated by the appearance of two peaks on the sedimentation diagram (Fig.16, curve 3), corresponding to the individual initial polyelectrolyte components#. It follows from the data presented that the disproportionation phenomenon is not observed in the homogeneous system, i.e. that the disproportionation is indeed closely related to the phase separation occurring on transition from region I to region II. Hence it also follows that, after the attainment of I_2 (Fig.14), the S-PEC still does not decompose fully into the individual components and dissolves actually in the form of the products of the incomplete interpolymer reaction. The complete dissociation of the polyelectrolyte complex into the LPE and the BPE occurs only in region III at high ionic strengths corresponding precisely to the appearance of two peaks on the sedimentation diagram for the solution.

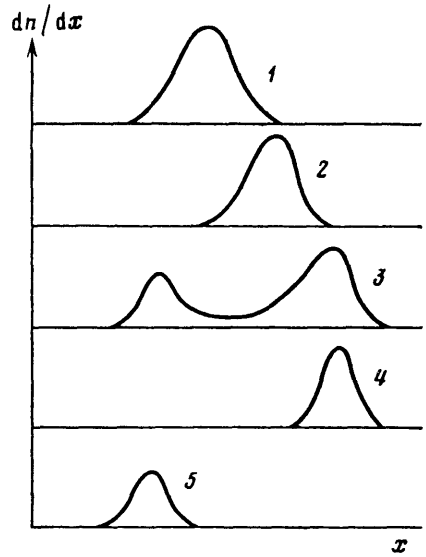


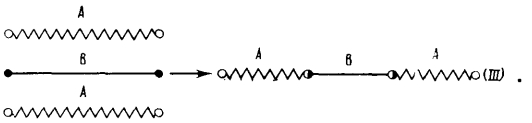
Figure 16. Sedimentation diagram for solutions of PMA-Na ($\bar{M}_w = 2.6 \times 10^5$)–PVP.$C_2H_5Br$ ($\bar{M}_w = 6 \times 10^4$) mixtures having the composition $Z = 0.14$ at different ionic strengths I(NaBr) [*1*) 0.2; *2*) 0.35; *3*) 0.48], PMA-Na (curve 4), and PVP.C_2H_5Br (curve 5). Concentration of solutions 0.3 wt.% at pH 7.5 and 20 °C. Time 60 min for a rate of spinning of 56000 min^{-1}.[55]

#In the experimental range of ionic strengths the individual polymeric components of the PMA-Na–PVP.C_2H_5Br system are not salted out, as happens, for example, in the sodium polystyrenesulphonate–polybenzylvinyltrimethylammonium chloride system[14].

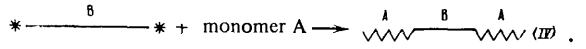
The other pairs of the electrostatically complementary polyelectrolytes taken in non-stoichiometric proportions and capable of forming the N-PEC (i.e. for $P_1 \gg P_2$) also behave analogously in aqueous salt media. This behaviour is caused by the thermodynamic reversibility of the interpolymer PEC formation reaction.

VI. PROSPECTS FOR THE DEVELOPMENT OF RESEARCH INTO AND THE POSSIBLE APPLICATIONS OF THE NEW CLASS OF POLYELECTROLYTES

The experimental data and considerations described in the review make it possible to regard the water-soluble N-PEC as an unusual variety of block-copolymers. Its unusual nature is manifested in the very synthesis of the N-PEC. In the classical chemistry of polymers one of two approaches is used for the synthesis of block-copolymers. According to the first of these, one synthesises initially the individual blocks A and B with the reactive groups at the ends, which are then linked to one another by a covalent bond as shown in the following scheme:



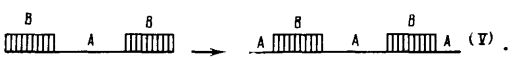
The second approach consists of the preliminary synthesis of blocks of, for example, type B whose terminal groups are capable of inducing the polymerisation of the corresponding monomer and the growth of blocks of type A:



In contrast to this, a fundamentally different approach is used in the synthesis of N-PEC, consisting in the lateral pairing of chemically complementary chains of different lengths.

The N-PEC is formed as a result of a very rapid ion-exchange reaction on simple mixing of aqueous solutions of the initial polyelectrolyte components. The process terminates almost instantaneously even at very high dilutions. The synthesis of the N-PEC can be achieved without any experimental tricks in the same working system where it is intended to function subsequently. The unusual nature and simplicity of the synthesis of hydrophilic-hydrophobic block macromolecules naturally lead to their new practical applications.

This is not all. In the block-copolymer synthesised by the usual method, the sequence of the alternation of the blocks and their lengths, i.e. the primary structure of the block macromolecules, are specified at the synthesis stage. Subsequently the structure can no longer be altered without the rupture of covalent chemical bonds. The macromolecules of the usual block-copolymer therefore attain thermodynamically optimum states in their interaction with one another and with the surrounding medium only by a change in their conformations, i.e. in their secondary structure. The situation is different in the case of the block N-PEC. By virtue of the reversibility of the reactions between the LPE and the BPE, the BPE chains can migrate along the LPE chains and can even move from one chain to another. Such migration actually implies an alteration of the relative lengths and number of hydrophilic and hydrophobic blocks in the complex macromolecule, for example, in accordance with the scheme



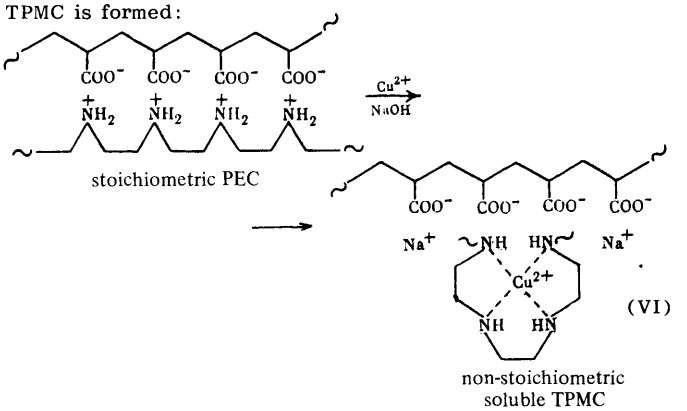
Consequently the complex block macromolecules of the N-PEC can "seek" thermodynamically optimum versions of the interaction with the surrounding medium not only by changing their secondary structure but also their primary structure. The unique ability of the N-PEC, which follows from this, which is to change as a function of the conditions its hydrophilic-hydrophobic balance and to become adjusted to the hydrophilic-hydrophobic balance of the surrounding species and surfaces, should also have important practical consequences, for example, in the solution of problems of flocculation or the stabilisation of colloidal systems.

The study of the structure and properties of N-PEC is extremely useful for the development of ideas concerning the behaviour of linear polyelectrolytes in classical highly disperse colloidal systems.

Non-stoichiometric polyelectrolyte complexes are of considerable interest also as the simplest model of polyelectrolyte complexes of biological origin, such as nucleoprotein, glycoprotein, etc. complexes. It has also been shown[47,58,59] that synthetic linear polyelectrolytes are capable of forming water-soluble complexes with oppositely charged proteins (albumin, globulins, etc.). Such complexes are characterised by a definite composition and molecular weight and are in many respects similar to the water-soluble N-PEC described above. They are of independent interest as fundamentally new biologically active macromolecular compounds, for example artificial antigens[60].

One rational explanation of the high physiological activity manifested by synthetic polyelectrolytes is based on the idea of their ability to interact cooperatively with oppositely charged biopolymers (nucleic acids, proteins, heparin, etc.) and also with cell membranes. Clearly, the polyelectrolyte complexes formed under these conditions can be both stoichiometric and non-stoichiometric.

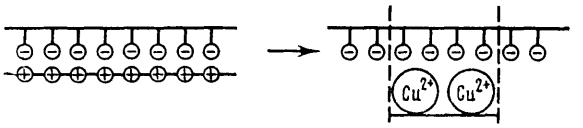
The reversible interpolymer reaction leading to the formation of an N-PEC can find applications in the creation of most varied functional macromolecular systems. In particular, we shall consider an example in which the ability of the PEC to bind strongly transition metal ions such as Cu^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, etc. is used. The ternary polymer–metal complexes (TPMC) thus formed can be both stoichiometric and water-soluble and non-stoichiometric and can be interconverted. The TPMC of linear polyethyleneimine (PEI), PA-Na, and Cu^{2+} has been studied in greatest detail[61–63]. If an aqueous solution of a bivalent salt is added to the insoluble PAA–PEI S-PEC with $\theta \cong 1$, the deposit of the polyelectrolyte complex is coloured an intense blue. For the ratio $[Cu^{2+}]:[\text{polyelectrolyte unit}] \cong 1:5$, a water-soluble TPMC is formed:



Each Cu^{2+} ion in the TPMC is then bound by coordinate bonds to four non-protonated amino-groups belonging to four neighbouring PEI units. The TPMC can therefore be characterised as a polyelectrolyte complex formed by the negatively

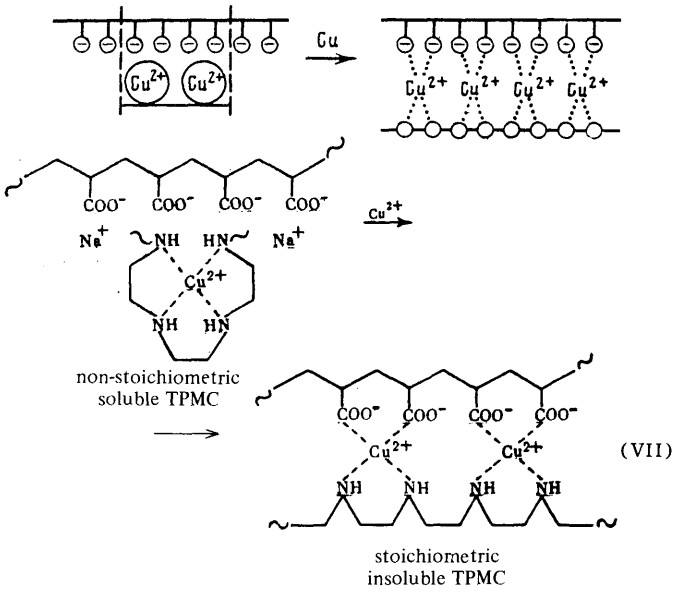
charged PA-Na chain and the positively charged chain of the copper complex of PEI. In the initial binary S-PEC there is one PEI unit per PAA unit. In contrast to this, in the TPMC for each two PAA units there are four PEI units, constituting the coordination sphere of the bivalent ion Cu^{2+}. Thus, on formation of the TPMC, the effective length of each PEI chain decreases. The PEI chains, as it were, "shrink" relative to the PA-Na chains. One-stranded sequences of the negatively charged PA-Na units are then liberated, as shown in Scheme *K*.

Scheme *K*



As a result, the TPMC acquires the block structure characteristic of the N-PEC and dissolves. However, if the addition of the copper salt to a solution of this TPMC is continued, then, for the ratio $[Cu^{2+}]/[\text{polyelectrolyte unit}] = 0.5$, phase separation occurs again. It is due to a rearrangement of the coordination sphere of the Cu^{2+} ion; in the presence of an excess of Cu^{2+}, only two PEI units remain in the TPMC molecule and two additional PAA units are incorporated. As a result, the TPMC acquires the continuous two-stranded structure characteristic of the S-PEC.[62] This is illustrated by reaction (VII) and Scheme *L*.

Scheme *L*



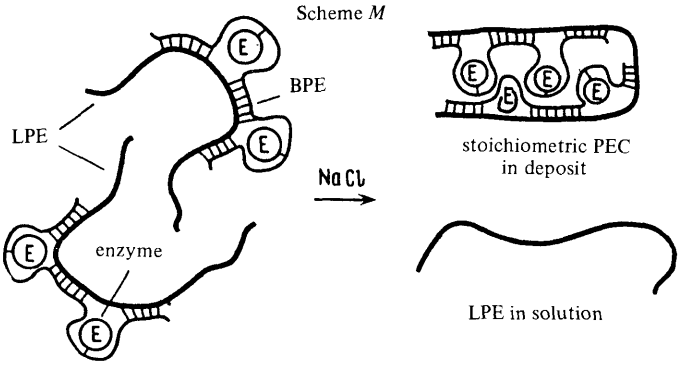
(VII)

The transformations of the TPMC as the concentration of transition metal ions in the surrounding solution is varied, described above, can be used, for example, for the creation of chemomechanical machines. The study of the above phenomena is of undoubted interest also for the creation of effective complex-forming ion-exchangers based on polyelectrolyte complexes.

Another example of functional macromolecular systems based on the N-PEC can be provided by the N-PEC–enzymes conjugated systems. The properties of penicillin amidase (*E*) from *E.coli*, incorporated in particles of the PMA-Na–$PVP.C_2H_5Br$ N-PEC, have been described[64]. The enzyme molecules were initially linked covalently to the BPE chains ($PVP.C_2H_5Br$) and then, using the procedures described above, the N-PEC was obtained ($\phi = 0.33$). The inclusion of the enzymes in the N-PEC species having an excess negative charge was accompanied by a considerable shift and distortion of the pH optimum in the enzyme activity induced by the Donnan exclusion effect. The activity of the enzyme hardly altered under these conditions. An important property of this three-component system is its ability to pass reversibly from the soluble to the insoluble state as the ionic strength of the solution is varied. The precipitation curve for the enzyme-containing PEC is very similar to the precipitation curve for the PMA-Na–$PVP.C_2H_5$ binary N-PEC having the same composition and presented in Fig.15.

The complete transition to the insoluble state takes place over a narrow range of salt concentrations (*I*), amounting to 0.01 M. The process is illustrated schematically in Scheme *M*.

Scheme *M*



The enzymes linked to the S-PEC formed are entrained together in the precipitate. It is remarkable that the formation of the deposit is accompanied by a virtually complete cessation of the enzymatic reaction. Since the phase separation process is reversible, it can be frequently repeated without loss of enzyme activity. Hence arises the possibility of creating self-regulating enzyme systems. If, for example, the enzymatic process involving the cleavage of the substrate leads to the formation of charged products, the ionic strength of the solution increases in the course of the reaction. After the attainment of an ionic strength I^* linked directly to the degree of conversion of the corresponding substrate, the N-PEC containing the enzyme is converted into the insoluble S-PEC. The enzymatic reaction should then stop independently. This has been demonstrated in relation to the hydrolysis of the sodium salt of benzylpenicillin by enzyme-containing N-PEC. The hydrolysis results in the formation of the sodium salt of 6-aminopenicillanic acid and the sodium salt of phenylacetic acid, which ultimately "stop" the reaction. By varying the initial ionic strength of the solution and (or) the composition of the N-PEC, it is possible to force the enzymatic reaction to stop automatically at any specified degree of conversion of the substrate.

* * *

The example presented naturally by no means exhaust all the theoretical and practical prospects for the employment of the N-PEC as a new class of water-soluble ionogenic macromolecular compounds. The very fact that the examples described refer to such varied and sometimes remote fields demonstrates convincingly the usefulness of further studies and research. Only the first steps have so far been taken in this direction.

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Advances in the Chemistry of Sulphur-containing Macroheterocycles

M.G.Voronkov and V.I.Knutov

Data on the methods of synthesis and structures of macroheterocyclic sulphides as well as their complexes with alkali and transition metal ions are surveyed and described systematically.
The bibliography includes 185 references

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I. INTRODUCTION

The chemistry of macrocyclic compounds arose more than half a century ago as a result of the studies of Ruzicka, who synthesised macrocyclic ketones in order to discover the nature of the active principle of substances with the odour of musk[1,2]. The further development of this branch of organic chemistry was promoted by the fundamental studies of Ziegler[3-7], Hansley[8], Prelog[9], Stoll[10,11], Shemyakin[12-14], and others[15-18] carried out between 1930 and 1960.

At the present time, the chemistry of macrocyclic compounds is developing very vigorously, owing to the recently discovered extensive possibilities for the employment of macrocycles not only in chemical practice but also in biology, medicine and engineering[19-21]. The syntheses of catenanes and rotaxanes, crown-ethers and cryptands, cyclophanes, *ansa*-compounds, annulenes, etc. have attracted much attention.

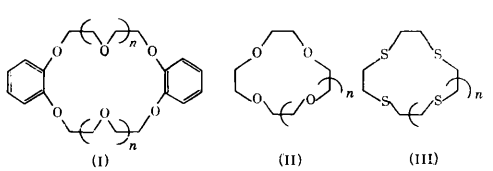
Macroheterocyclic compounds, namely crown-ethers, cryptands, and similar substances, whose study is closely related to the discovery of natural macroheterocyclic compounds, occupy a special place in the chemistry of macrocycles. The study of natural macroheterocycles—peptides, depsipeptides, and depsides—led to the discovery of their ability to form stable complexes with alkali and alkaline earth metals and to transfer these cations through natural and synthetic membranes. Such compounds have been called membranoactive complexones or ionophores[19]. The development of the chemistry of synthetic macroheterocyclic complexones is associated with the possibility of obtaining compounds whose properties are analogous to those of natural macroheterocycles. They can be regarded as simplified models of natural macroheterocyclic ionophores. Individual examples of synthetic macroheterocycles have been obtained by various groups of investigators[22-27], but the vigorous development of the chemistry of macroheterocycles has been stimulated by Pedersen's studies on the synthesis and complex formation reactions of macroheterocyclic polyethers with alkali and alkaline earth metal salts[28]. The vigorous development of the chemistry of macroheterocycles is indicated by the publication of recent monographs[19-21,29,30] and general reviews[31] and reviews devoted to individual classes of macroheterocycles: ethers[32], esters[33], amines[34], sulphides[35], heterocyclophanes[36], and other compounds of a similar type[37-40].

This review deals with studies on sulphur-containing macroheterocyclic compounds published in 1974–1980 (earlier investigations have been reviewed elsewhere[35]).

II. MACROHETEROMONOCYCLIC SULPHIDES

1. Macropolythiamonocyclanes

In 1967 Pedersen synthesised aromatic macroheterocyclic polyethers (I) and called them crown-ethers[28]. He observed that these compounds form stable complexes with alkali and alkaline earth metal cations as well as ammonium and silver cations. Crown-ethers are obtained by the condensation of 1,2-dihydroxyarenes with the corresponding α,ω-dichloro-derivatives in boiling 1-butanol in the presence of alkali metal hydroxides; in individual instances the yields reach 62%.

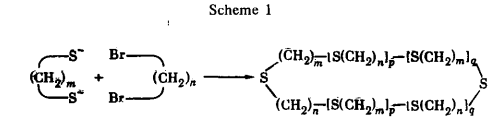


(I) (II) (III)

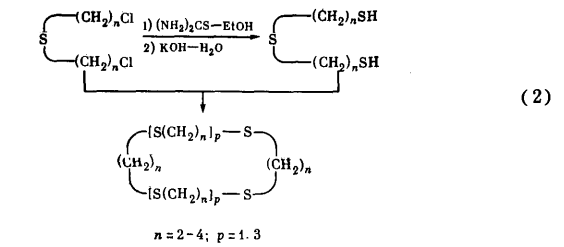
Instead of dichloro-derivatives, it is possible to employ ditosyl derivatives; heterocyclic polyethers of type (II) have been obtained from them in yields of 45%.[41-43,57] The high yields of crown-ethers can be accounted for by the "template" effect arising on coordination of alkali metal ions to the oxygen atoms in the cyclisation of the polyether.

Under analogous conditions, macropolythiamonocyclanes (III) are formed in only a low yield (less than 2%)[44] owing to the absence of the "template" effect because of the weak affinity of the sulphur atoms for alkali metal ions[45]. High dilution of the reaction mixture made it possible to improve the method of synthesis of macropolythiamonocyclanes[45,46]. The proposed methods (see Scheme 1) make it possible to synthesise macropolythiamonocyclanes in yields up to 35% (Table 1).

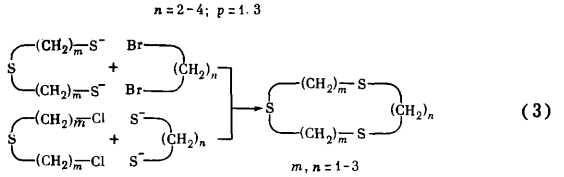
Scheme 1



$m, n = 3-5$; $p, q = 0,1$ (1)



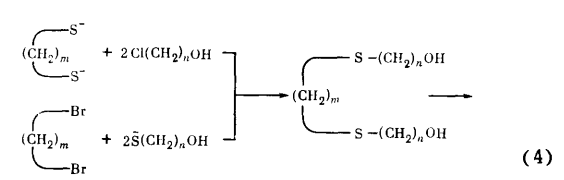
(2)



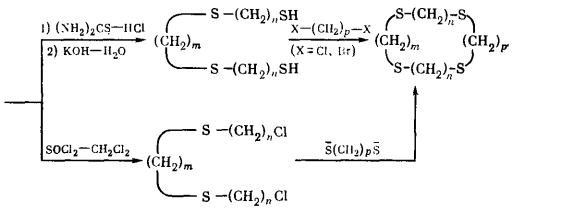
$n = 2-4$; $p = 1.3$

(3)

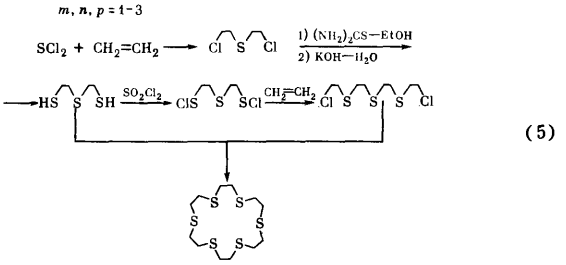
$m, n = 1-3$



(4)



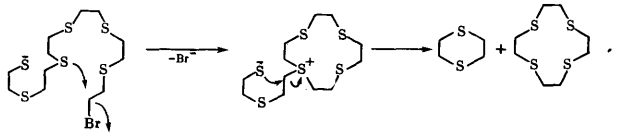
$m, n, p = 1-3$



(5)

Method (1) is most suitable for the synthesis of tetrathia- and hexathia-cyclanes in which the sulphur atoms are separated by tetra- and penta-methylene bridges. On the other hand, methods (3) and (5) lead to the maximum yields of macropolythiacyclanes consisting of alternating SCH_2CH_2 units.

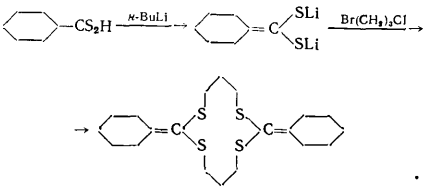
1,4-Dithiane and 1,4,7,10-tetrathiacyclododecane were unexpectedly obtained in reactions (1) and (3) together with 1,4,7,10,13,16-hexathiacyclo-octadecane. This is due to the formation of a cyclic sulphonium ion as a result of intramolecular cyclisation[45]:



When methods (2), (4), and (5) are used, the amount of side products is reduced to a minimum.

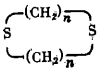
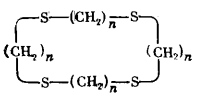
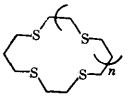
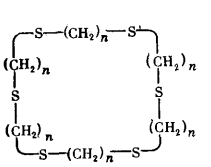
The kinetics of the formation of complexes by the Cu^{2+} ion with macrocyclic sulphides have been investigated and the influence of the solvent and the ring size has been considered[47-51]. The possibility of using these compounds as extractants for silver and mercury salts has been studied[52-55].

2,8-Bis(cyclohexylidene)-1,3,7,9-tetrathiacyclododecane (IV) has been obtained from cyclohexanedithiocarboxylic acid[56]:

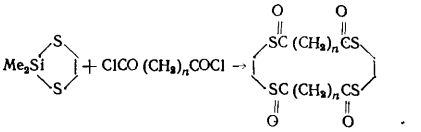


(IV)

Table 1. Macropolythiamonocyclanes.

Compound	n	M.p., °C	Yield, %	References
	5 6	81—82.5 77—78	0.8 1.4	[45] [45]
	3 4 5 6	57.5—59 31—32 33—33.5 30—32	19.5 3.9 5.3 3.9	[45, 49—51] [45, 51] [45] [45]
III	1 2 3	224—225 97.5—99 91—93	6.3 11.0 35.0	[45, 46, 49, 50] [45, 46, 49, 50] [45, 55]
	1 3 5	121—122.5 64—65 —	22.1 9.7 —	[45, 49—51, 53, 55] [45, 49] [53, 54]
	3 4 5 6	29—30 67—70 36.5—38 56—59.5	15.1 1.7 6.8 3.2	[45] [45] [45] [45]

The interaction of the highly reactive 2,2-dimethyl-2-sila-1,3-dithiacyclopentane with dicarboxylic acid dichlorides has been used to synthesise macroheterocyclic thiolactones (V):[57,58]



$n = 3, 5, 7, 8$ (V)

Several sulphur-containing annulenes have been obtained by the oxidative coupling reaction of diacetylenic sulphides[60, 61]. The interaction of bis[(triphenylphosphonia)methyl] sulphide dibromide with *o*-ethynylbenzaldehyde led to the synthesis of the corresponding diacetylenic derivative whose

oxidation in the presence of copper acetate in pyridine resulted in the formation of the macroheterocycle (VI):

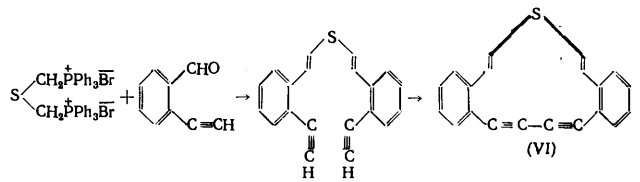
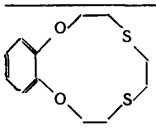
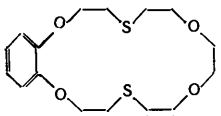
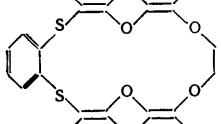
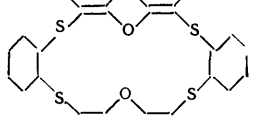
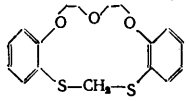
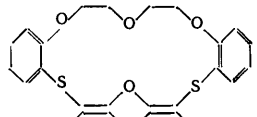
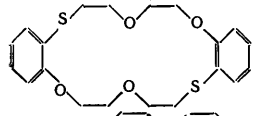
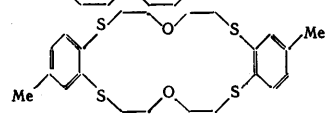
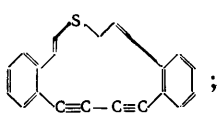


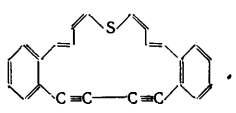
Table 2. Thiacrown-ethers.

Compound	M.p., °C	Yield, %
	92	34
	91	1.0
	*	56
	*	30
	150—153	3.0
	143—144	15
	113.5	5.0
	147	6.0

*An oil is formed.

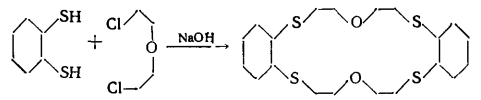
Compounds (VII) and (VIII) have been obtained analogously:


(VII)


(VIII)

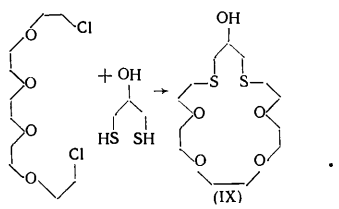
2. Macro-oxathiacyclanes

Crown-ethers containing sulphur atoms in the ring together with oxygen atoms were first synthesised by Pedersen[59,62], who also showed that, when oxygen atoms are substituted by sulphur atoms, the complex-forming properties of the crown-ethers in relation to potassium and sodium ions are weakened, while the complexes with silver ions are in fact strengthened. Thiacrown-ethers have been obtained by the condensation of aromatic 1,2-dithiols or *o*-mercaptophenol with aliphatic α,ω-dihalogeno-derivatives. The reaction of *o*-dihalogenoarenes with aliphatic α,ω-dithiols can also be used. *trans*-Cyclohexane-1,2-dithiol reacts with di(β-chloroethyl) ether analogous to 1,2-dithiols, forming 5,18-dioxa-2,8,15,21-tetrathiatricyclo[20,4,0,0^{9,14}]hexacosane:

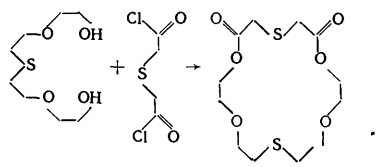


The thiacrown-ethers synthesised are listed in Table 2.[62]

The reaction of aliphatic α,ω-dithiols with dichlorohydrins has also been used to synthesise thiacrown-ethers (Table 3).[63] For example, the macroheterocycle (IX) has been obtained (in 80% yield) by the reaction of 1,14-dichloro-3,6,9,12-tetraoxatetradecane with 1,3-dimercapto-2-propanol:

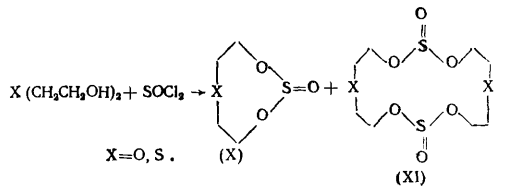


More than twenty thiacrown-ethers containing ester groups in the ring have also been obtained[64–68]. Sulphur-containing macroheterocyclic di- and tetra-oxa-esters have been synthesised by the interaction of oligo(ethylene thioglycols) or by the corresponding dithiols with the dichlorides of dicarboxylic acids under the conditions of high dilution (Table 3). The dichlorides of oxalic, malonic, succinic, and 3-thiaglutaric acids were used, for example:



Interest in macrolactones was aroused primarily by the possibility of using them as perfumes[33]. In connection with the discovery of the natural macrocyclic antibiotic valinomycin, containing carbonyl groups in the ring and exhibiting unique complex-forming properties in relation to alkali metal ions[19], nowadays these compounds attract attention as complex-forming agents. It was found that they exhibit a high complex-forming activity in relation to alkali and alkaline earth metal ions. Sulphur-containing macroheterocycles of this type form complexes with Na^+, K^+, Ag^+, Rb^+, Cs^+, and Ba^{2+} ions[69–72].

The reaction of diethylene glycol or β-thiodiglycol with thionyl chloride leads to the formation of heterocycles (X) of moderate size and macroheterocycles (XI):[73]



;

Table 3. Sulphur-containing di- and tetra-oxo-crown-ethers.

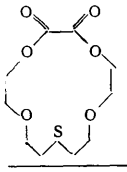
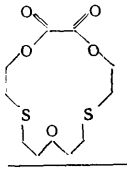
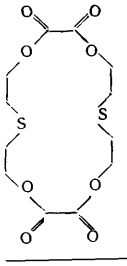
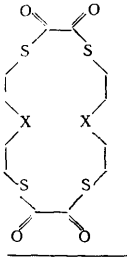
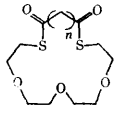
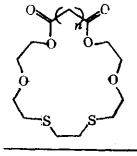
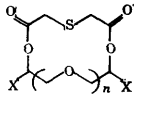
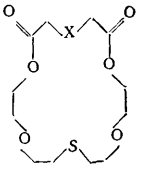
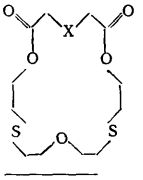
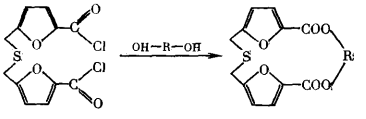
Compound	*n*	X	M.p., °C	Yield, %	Refs.
	—	—	88—90	5.7	[67]
	—	—	45	7.7	[67]
	—	—	195—203	14	[67]
	—	O	207—210	67	[67]
	—	S	108—109	62	[67]
	1	—	*	—	[64]
	2	—	*	—	[64]
	1	—	*	85	[64]
	2	—	*	80	[64]
	1	H	93.5—94.5	4.8	[65]
	2	H	85.5—86.5	2.3	[65]
	3	H	43.5—44.5	20	[65]
	1	Et	96.5—97.5	6	[68]
	2	Et	121.5—122.5	20	[68]

Table 3 (cont'd).

Compound	*n*	X	M.p., °C	Yield, %	Refs.
	—	O	113.5—115	35	[65]
	—	S	106—107	11	[65]
	—	O	36—36.5	20	[65]
	—	S	*	31	[65]

*An oil is formed.

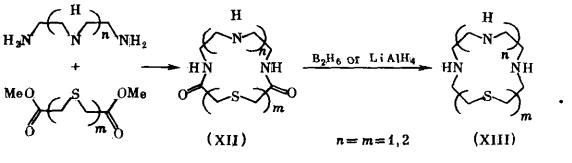
A series of sulphur-containing macroheterocycles have been synthesised using the dichloride of 5,5'-[thiobis(methylene)]-bisfuran-2-carboxylic acid as the key reagent[74]. A wide variety of diols (catechol, resorcinol, hydroquinone, monoethylene and triethylene glycols, 2,2-dimethylpropane-1,3-diol, propane-1,2-diol, 2,4-dimethyl-3-oxapentane-1,5-diol, *cis*- or *trans*-but-2-ene-1,4-diol, and but-2-yne-1,4-diol) as well as ethane-1,2-dithiol have been used as the second reagent (Table 4):



The reaction is carried out in the presence of lithium hydride in dimethylformamide with prolonged refluxing (20 h); the yields of the macroheterocycles are 11—77%.

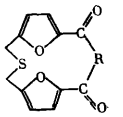
3. Macrothiazacyclanes

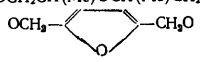
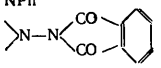
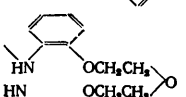
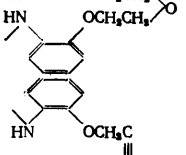
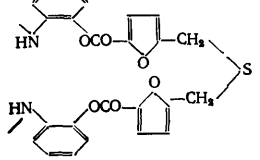
The general method of synthesis of macrothiazacyclanes is based on the aminolysis of the readily available dimethyl esters of thia-alkane-α,ω-dicarboxylic acids by polyethylenepolyamines and subsequent reduction of the resulting macroheterocyclic amides[75]:



Sulphur-containing macroheterocyclic diamides (XII) have been obtained in yields of 15.4—40.9% by heating the reactant for 3—7 days without high dilution or protection of the secondary amino-group. Successful cyclisation takes place by virtue of the different reactivities of the NH_2 and NH groups in the initial polyethylenepolyamines. The macrocyclic diamide can be reduced by lithium tetrahydroaluminate or diborane in tetrahydrofuran (THF), the yields of the corresponding macrothiazacyclanes (XIII) amounting to 60—80%.

Table 4. Macroheterocyclic derivatives of 5,5′-[thiobis-(methylene)]bisfuran-2-carboxylic acid.



R	M.p., °C	Yield, %	Refs.
$O(CH_2)_2O$	157—158	16	[74]
$[O(CH_2)_2]_3O$	212—214	54	[74]
$[O(CH_2)_2]_4O$	190—191	13	[74]
$[O(CH_2)_2]_5O$	215—217	28	[74]
$[O(CH_2)_2]_6O$	218—219	36	[74]
$O(CH_2)_2S(CH_2)_2O$	200—201	57	[74]
o-OC_6H_4O	46—48	77	[74]
m-OC_6H_4O	69—70	30	[74]
p-OC_6H_4O	66—68	11	[74]
$S(CH_2)_2S$	218—220	29	[74]
cis-$OCH_2CH=CHCH_2O$	192—193	70	[74]
trans-$OCH_2CH=CHCH_2O$	185—186	30	[74]
$OCH_2C\equiv CCH_2O$	216—218	60	[74]
$O(CH_2)_6O$	212—213	45	[74]
$OCH_2CH(Me)O$	185—186	53	[74]
$OCH(Me)CH(Me)O$	205—206	50	[74]
$OCH(Me)CH_2CH_2O$	214—215	65	[74]
$OCH_2C(Me)_2CH_2O$	216—217	52	[74]
$OCH_2CH(Me)OCH(Me)CH_2O$	218—220	37	[74]
	310—312	57	[87]
$OCH_2CH_2OCH_2C\equiv CCH_2OCH_2CH_2O$	218—220	43	[87]
$O(CH_2CH_2O)_2CH_2C\equiv CCH_2(OCH_2CH_2)_2O$	220—221	36	[87]
$O(CH_2CH_2O)_3CH_2C\equiv CCH_2(OCH_2CH_2)_3O$	217—218	12	[87]
trans-$OCH_2CH_2OCHCH=CHCH_2OCH_2CH_2O$	223—224	40	[87]
trans-$O(CH_2CH_2O)_2CH_2CH=CHCH_2(OCH_2CH_2)_2O$	210—211	32	[87]
$NH(CH_2)_2NH$	210—212	50	[86]
$NH(CH_2)_3NH$	72—73	22	[86]
$NH(CH_2)_6NH$	87—88	50	[86]
o-NHC_6H_4NH	197—198	97	[86]
m-NHC_6H_4NH	204—205	80	[86]
p-NHC_6H_4NH	224—225	91	[86]
$NH(CH_2)_2S(CH_2)_2NH$	45—46	93	[86]
NPh	184—185	97	[86]
	88—89	62	[86]
	230—231	53	[87]
	218—219	69	[87]
	225—227	83	[87]

Data on the synthesis of macroheterocycles containing alkyl, arylalkyl, or functional groups at the nitrogen or carbon atoms have been published with increasing frequency in recent years[32,40]. Such compounds have been used to form complexes with alkali and alkaline earth metal ions and to investigate complex formation kinetics, ion transfer through natural and synthetic membranes, and catalysis of interfacial transfer. Cryptands and their polymacroheterocyclic analogues have been synthesised from macroheterocycles with functional groups. Macroheterocycles with functional groups have been investigated as biologically active substances. After being immobilised in polymeric materials, such heterocycles are used as new heterogeneous catalysts. Finally they can be employed as reactive reagents in organic synthesis.

A new approach to the synthesis of open-chain and macroheterocyclic diamines with arylalkyl and functional group substituents has been discovered[76–80]. The synthesis of *N*-substituted open-chain diamines is based on the reaction of *N*-substituted aziridines with α,ω-dithiols. At 60 °C in methanol α,ω-dithiols react with two moles of aziridine, forming open-chain diamines (XIV). The analogous reaction in an aprotic solvent, for example, benzene, leads to the monoadducts (XV), which are oxidised by atmospheric oxygen to the corresponding disulphides (XVI) (Scheme 2):

Scheme 2

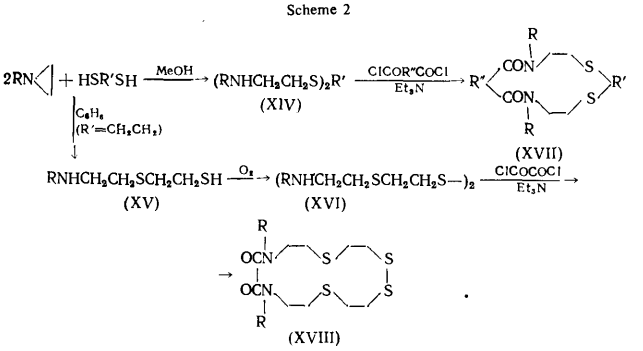
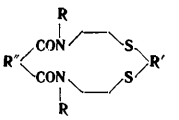


Table 5. Sulphur-containing macroheterocyclic diamides.



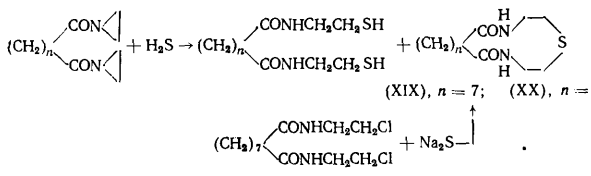
R	R′	R″	M.p., °C	Yield, %	Refs.
H	CH_2CH_2	$CH_2(CH_2)_2CH_2$	170—171	65	[80]
$PhCH_2CH_2$	CH_2CH_2	$CH_2(CH_2)_2CH_2$	134—135	70	[80]
$MeOCOCH_2CH_2$	CH_2CH_2	$CH_2(CH_2)_2CH_2$	105—107	68	[80]
$NCCH_2CH_2$	CH_2CH_2	$CH_2(CH_2)_2CH_2$	184—185	70	[80]
H	CH_2CH_2	*o*-C_6H_4	181—182	66	[76—78]
$PhCH_2CH_2$	CH_2CH_2	*o*-C_6H_4	190—191	70	[80]
$MeOCOCH_2CH_2$	CH_2CH_2	*o*-C_6H_4	*	70	[76—78]
$NCCH_2CH_2$	CH_2CH_2	*o*-C_6H_4	*	70	[80]
H		*o*-C_6H_4	135—136	50	[79]
$MeOCOCH_2CH_2$		*o*-C_6H_4	72—73	55	[79, 80]
$MeOCOCH_2CH_2$	CH_2CH_3	$CH_2CH_2SCH_2CH_2SCH_2CH_2$	*	60	[80]
H	$CH_2CH_2SSCH_2CH_2$	—	135	80	[76—78]
$MeOCOCH_2CH_2$	$CH_2CH_2SSCH_2CH_2$	—	*	60	[80]

*An oil is formed.

The cyclisation of the diamines (XIV) and (XVI) with dicarboxylic acid dichlorides has been investigated with the aim of synthesising macroheterocyclic compounds containing arylalkyl and functional groups at the nitrogen atom. The reaction is carried out in dry benzene at high dilution. The resulting *N*-unsubstituted macroheterocycles as well as the macroheterocyclic compounds (XVII) and (XVIII), containing

phenylethyl, methoxycarbonylethyl, and cyanoethyl groups are presented in Table 5.

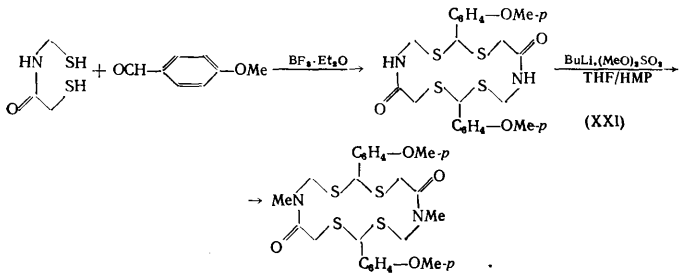
The reaction of bis-*N*-ethyleneamides of azelaic and sebacic acids with an excess of hydrogen sulphide led to the isolation of the macrocyclic sulphides (XIX) and (XX) together with the bis(β-mercaptoethyl)diamides of the corresponding dicarboxylic acids[81]:



(XIX), $n = 7$; (XX), $n = 8$

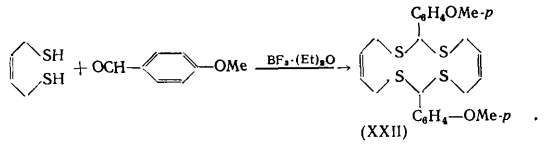
The macrocyclic compounds are apparently the products of the intramolecular opening of the aziridine rings by the mercapto-group in the intermediate *N*,*N*-ethylene-*N*'-(β-mercaptoethyl)diamides of azelaic and sebacic acids. The cyclic sulphide (XIX) has also been synthesised by the reaction of the bis(β-chloroethyl)diamide of azelaic acids with sodium sulphide.

The reaction of the *N*-(mercaptomethyl)amide of thioglycolic acid with anisaldehyde leads to the formation of the macrocycle (XXI):[82]



(XXI)

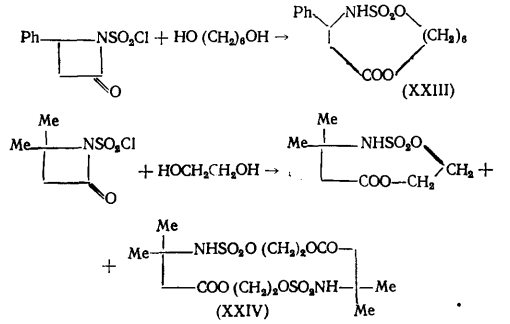
The macroheterocycle (XXII) has been obtained analogously by the reaction of 1,4-dimercaptobut-2-ene with anisaldehyde:



(XXII)

4. Macro-oxathiazacyclanes

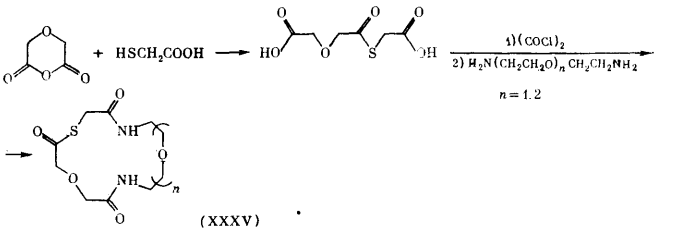
The reaction of *N*-chlorosulphonyl-β-lactams with glycols leads to the formation of the new macroheterocycles (XXIII) and (XXIV):[83-84]



(XXIII)

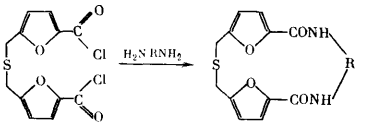
(XXIV)

Oxygen- and nitrogen-containing macroheterocyclic sulphides have been synthesised from 5-oxo-3-oxa-6-thiahexanedicarboxylic acid, which is the product of the reaction of the anhydride of diglycolic acid with thioglycolic acid[85]. The dicarboxylic acid obtained was converted by treatment with oxalyl chloride into the corresponding acid dichloride whose reaction with 1,5-diamino-3-oxapentane or 1,8-diamino-3,6-dioxaoctane at high dilution leads to the macroheterocycle (XXXV) in 30–35% yield:

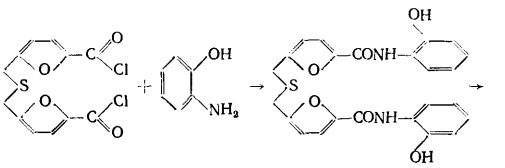


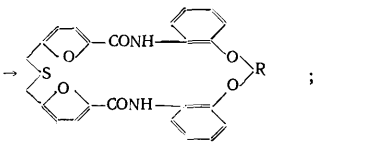
(XXXV)

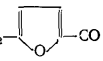
The macroheterocyclic amides have been obtained analogously in higher yields using the dichlorides of 5,5'-[thiobis(methylene)]bisfuran-2-carboxylic acid and aliphatic or aromatic diamines (Table 4):[86]



R=$(CH_2)_2$, $(CH_2)_3$, $(CH_2)_6$, $(CH_2)_2S(CH_2)_2$, *o*-C_6H_4, *m*-C_6H_4, *p*-C_6H_4





R=$CH_2CH_2OCH_2CH_2$, $CH_2C{\equiv}CCH_2$, CO–  –CH_2SCH_2–  –CO

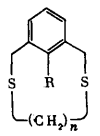
The reaction of the dichloride of 5,5'-[thiobis(methylene)]-bisfuran-2-carboxylic acid with o-aminophenol leads to the corresponding diamide, whose subsequent interaction with dichlorides (refluxing in the presence of potassium hydroxide for 25–30 h) leads to the formation of sulphur-containing macroheterocycles in 53–83% yields (Table 4).[87]

III. THIA- AND POLYTHIA-CYCLOPHANES

1. Sulphur-containing Cyclophanes

Cyclophanes are cyclic compounds containing one or several benzene rings connected by polymethylene bridges in the *ortho*-, *meta*-, or *para*-positions. Interest in these compounds arose in connection with the possibility of investigating the steric interaction of substituents, transannular effects, the dependence of the barrier to the rotation of the benzene rings on the length of the methylene bridge, etc.

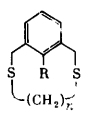
A large series of dithiacyclophanes (XXVI), containing from 3 to 12 methylene groups in each aliphatic bridge incorporating a wide variety of intra-annular substituents in the benzene ring, have been synthesised (Table 6).



(XXVI)

n=3–12; R=Ph, I, NH_2, NO_2, OH, OMe, SMe, SOMe, SO_2Me

Table 6. Dithiametacyclophanes

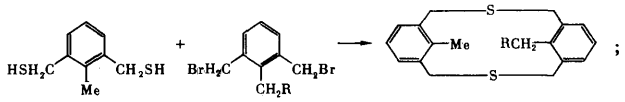


n	R	M.p., °C	Yield, %	Refs.	n	R	M.p., °C	Yield, %	Refs.
3	NO_2	145–148	4	[88]	8	CO_2Me	80–82	34	[88]
4	NO_2	102	45	[88]	9	CO_2Me	*	39	[88]
5	NO_2	97	21	[88]	10	CO_2Me	*	57	[88]
6	NO_2	116	42	[88]	11	CO_2Me	*	46	[88]
7	NO_2	94	20	[88]	12	CO_2Me	*	49	[88]
8	NO_2	80	48	[88]	4	SMe	100–103	3	[88]
9	NO_2	41–43	13	[88]	6	SMe	101–104	15	[88]
10	NO_2	78–80	2	[88]	8	SMe	*	44	[88]
8	I	44–47	17	[91]	9	SMe	*	53	[88]
9	I	<20	9	[91]	10	SMe	*	38	[88]
10	I	<20	11	[91]	4	SOMe	154–156	29	[89]
6	OH	113–114	4	[91]	6	SOMe	148–150	38	[89]
7	OH	108–110	5	[91]	8	SOMe	128–130	19	[89]
4	NH_2	94–95	39	[91]	9	SOMe	124–125	37	[89]
5	NH_2	76–77	56	[91]	10	SOMe	112–114	22	[89]
6	NH_2	79–80	67	[91]	11	SOMe	97–100	11	[89]
7	NH_2	77–78	60	[91]	4	SO_2Me	144–147	5	[88]
8	NH_2	42–44	55	[91]	6	SO_2Me	118–120	29	[88]
9	NH_2	<–16	73	[91]	8	SO_2Me	177–180	11	[88]
6	NHAc	161–164	60	[91]	10	SO_2Me	154–156	10	[88]
8	NHAc	110	98	[91]	11	SO_2Me	128–130	19	[88]
9	NHAc	90–91	89	[91]	12	SO_2Me	80–82	18	[88]
8	$N(Ac)_2$	126	94	[91]	4	Ph	133–134	22	[88]
9	$N(Ac)_2$	110–111	96	[91]	5	Ph	109–110	23	[88]
6	CO_2Me	102–103	30	[88]	6	Ph	126–127	9	[88]
					7	Ph	*	22	[88]
					8	Ph	62–64	18	[88]
					10	Ph	44–46	11	[88]
					12	Ph	*	11	[88]

*An oil is formed.

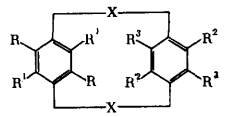
Cyclophanes with oxygen and sulphur atoms in the polymethylene bridges have also been obtained[88–91,111,117]. It has been shown by NMR that the steric requirements of an NO_2 group in these macrocyclic compounds are somewhat less stringent than those of a methyl group. CO_2Me and SO_2Me Groups are more bulky than NO_2 and SMe, but the bulk of an SMe group is greater than that of an OMe group. An SOMe group occupies an intermediate position between SO_2Me and SMe; the bulk of an NH_2 group is similar to that of a hydroxy-group. Both these substituents (NH_2 and OH) are more bulky than a fluorine atom linked to the aromatic ring, but are appreciably smaller than a chlorine atom or SMe and NO_2 groups. The general steric requirements of an iodine atom linked to an aromatic ring are more stringent than those of a chlorine or bromine atom but are comparable to those of an SMe group[88–91].

Dithiametacyclophanes containing intra-annular alkyl, alkenyl, and alkoxy-groups in the benzene ring have been synthesised[92,93]. They have been obtained by the interaction of 2,6-bis(mercaptomethyl)toluene with 2,6-bis(bromomethyl)-substituted benzenes; the yields of the macroheterocycles (XXVII) are 53–80%:



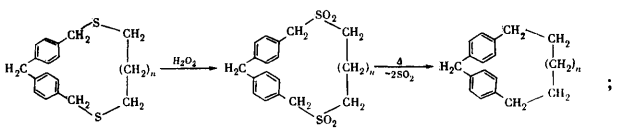
R = n-Pr, $CH_2CH{=}CH_2$, CH_2OMe. (XXVII)

Dithiaparacyclophanes containing bromine atoms, methoxy-groups, or cyano-groups in the benzene ring have been synthesised by the reaction of the corresponding 1,4-bis-(mercaptomethyl)benzenes with 1,4-bis(bromomethyl)-benzenes[94,95]:



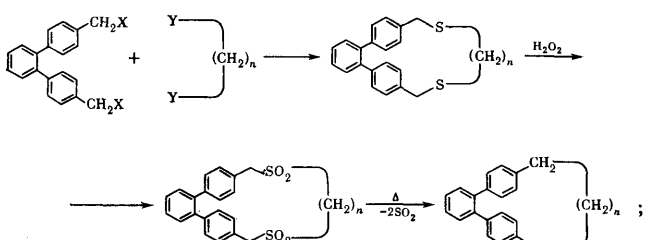
X = S, SO_2; R = R^1 = R^3 = H; X = S, SO_2; R = R^3 = H, R^1 = CN, R^3 = OMe; X = S, SO_2; R = R^3 = H, R^1 = CN, R^2 = OMe; X = S; R = Br, R^1 = R^3 = OMe, R^3 = H.

In recent years the pyrolysis of cyclic sulphones has been used widely for the synthesis of cyclophanes. The synthesis of sterically hindered paracyclophanes (XXVIII) has been achieved in this way[96]:



n=1–3. (XXVIII)

A series of cyclophanes containing two or three benzene rings in their molecules has been obtained[97–101]. The main method of synthesis of the initial dithiacyclophanes involves the reaction of the corresponding dibromides with dithiols (Table 7):

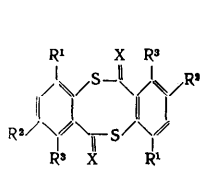


n=2–10, X=Br, SH, Y=SNa, Br.

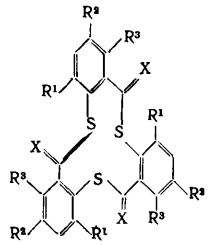
An analogous method has been used to synthesise dithiabiphenylophanes[102–105], dithiabiphenylnaphthalinophanes[123–131], dithiaphenanthrenophanes, and dithiaphenanthrenonaphthalinophanes[136–138] (Table 8).

The homocyclisation of *o*-mercaptobenzyl chloride under the influence of sodium hydroxide and of methyl-substituted *o*-mercaptobenzoic acids under the influence of P_5O_{10} at a high

dilution proceeds with formation of both cyclic dithiaorthocyclophanes (XXIX) of moderate size and the macrocyclic trithiaorthocyclophanes (XXX) (yield 6.4–10%).[107,116,122]



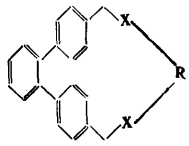
(XXIX)



(XXX)

$X = H_2$, $R^1 = R^2 = R^3 = H$; $X = O$, $R^1 = Me$, $R^2 = R^3 = H$;
$X = O$, $R^1 = R^3 = H$, $R^2 = Me$;
$X = O$, $R^1 = R^2 = H$, $R^3 = Me$; $X = O$, $R^1 = R^3 = Me$, $R^2 = H$.

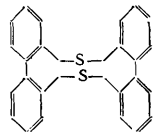
Table 7. Dithiatriphenylenophanes[98]



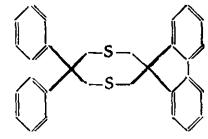
R	M.p., °C	Yield, %	M.p., °C	Yield, %
	X=S		X=SO$_2$	
$CH_2CH_2OCH_2CH_2$	157—159	14	297—299	90
$CH_2(CH_2OCH_2)_2CH_2$	117—118	19	232—234	60
$CH_2(CH_2OCH_2)_3CH_2$	110—112	7	235—238	87
$CH_2CH_2SCH_2CH_2$	110—111	9	—	—
$CH_2CH_2SO_2CH_2CH_2$	—	—	330—332	80
o-$CH_2C_6H_4CH_2$	192—195	12	355*	80
m-$CH_2C_6H_4CH_2$	175—177	17	323—324	73
2-$CH_2C_6H_3(NO_2)CH_2$-6	190—193	9	295*	74
2-$CH_2C_6H(Me_3$-1,3,5$)CH_2$-6	241—242	19	350*	80
p-$CH_2C_6H_4CH_2$	172—175	17	337—338	82

*Decomposition temperature.

The cyclocondensation of (*o*-$BrCH_2C_6H_4)_2$ with (*o*-$HSCH_2C_6H_4)_2$ leads to the formation of a mixture of the sulphur-containing macroheterocycles (XXXI) and (XXXII):[108]



(XXXI)



(XXXII)

Table 8. Sulphur-containing biphenylo-, naphthaleno-, and anthraceno-phanes.

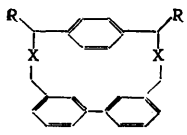
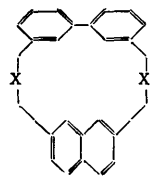
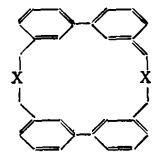
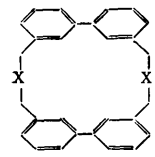
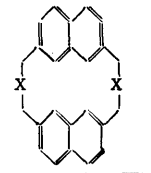
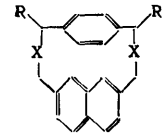
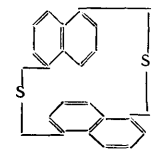
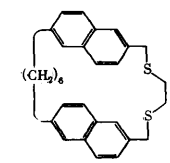
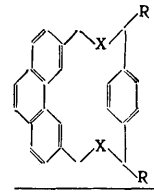
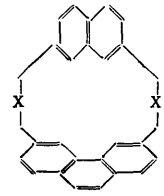
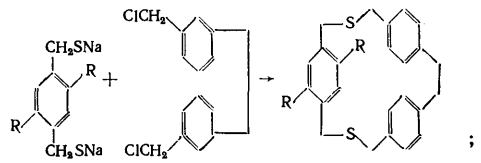
Compound	X	R	M.p., °C	Yield, %	Refs.
	S	H	213—215	49	[102]
	S	Me	180—181	63	[102]
	SO_2	H	>300	100	[102]

Table 8 (cont'd).

Compound	X	R	M.p., °C	Yield, %	Refs.
	S	—	234—235	49	[103, 123]
	$^+SMeBF_4^-$	—	>300	—	[103, 123]
	SO_2	—	>350	—	[103]
	S	—	266—268	74	[104]
	$^+SMeBF_4^-$	—	>300	—	[104]
	SO_2	—	>300	—	[104]
	S	—	249—251	73	[105]
	$^+SMeBF_4^-$	—	205—207*	~100	[105]
	SO_2	—	320	95	[105]
	S	—	240—244	—	[124, 137]
	$^+SMeBF_4^-$	—	>210	93	[124]
	SO_2	—	>300	89	[124]
	S	H	239—241	50	[125, 126]
	S	Me	245—246	55	[125, 126]
	$^+SMeBF_4^-$	H	>340	~100	[125, 126]
	$^+SMeBF_4^-$	Me	>360	~100	[125, 126]
	SO_2	H	>340	97	[125]
	—	—	281—283	6	[129]
	—	—	190—192	56	[131]
	S	H	248—250	52	[136, 137]
	$^+SMeBF_4^-$	H	>300	~100	[137]
	SO_2	H	>300	26	[137]
	S	Me	208—210	36	[137]
	$^+SMeBF_4^-$	Me	300*	90	[137]
	S	—	249—250	60	[138]
	$^+SMeBF_4^-$	—	>300	94	[138]

*Decomposition temperature.

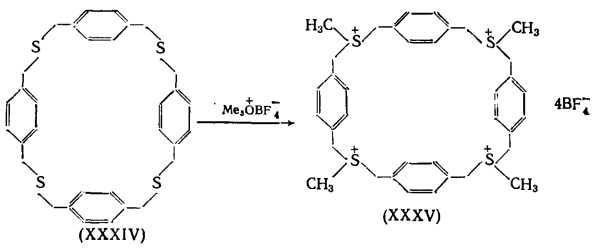
In order to investigate the effects of the internal rotation of the benzene rings in macrocyclophanes, dithiatriparacyclophanes (XXXIII) with various substituents in the *para*-position of the benzene ring have been obtained[109]:



R = H, F, Cl, Me, OMe . (XXXIII)

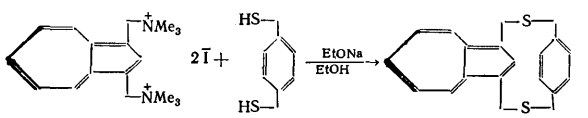
They were synthesised by the reaction of sodium dithiolates with 1,2-bis(4-chloromethylphenyl)ethane in a benzene-alcohol solution at high dilution; the yields of the dithiacyclophanes (XXXIII) are 15–55%.

When the tetrasulphide (XXXIV) was treated with $Me_3\overset{+}{O}\overline{B}F_4$, the water-soluble tetrathiaparacyclophane (XXXV) was isolated[110]:



(XXXIV) (XXXV)

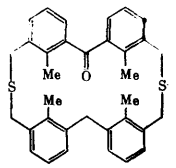
Using the high dilution technique, dithia-azulenoparacyclophane (XXXVI) was synthesised by the reaction of 1,3-bis(trimethylammoniamethyl)azulene di-iodide with 1,4-bis(mercaptomethyl)benzene (yield 40%):[114]



(XXXVI)

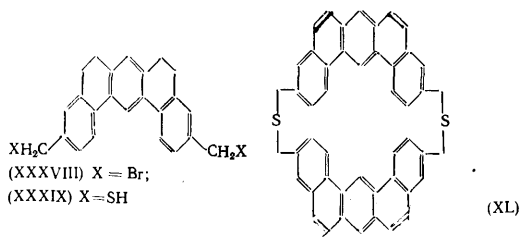
Two-layer and three-layer cyclophanes have been obtained in order to investigate the transannular interaction between the π electrons of the benzene ring[106,112,113,118–120,149]. The method of their synthesis is based on the pyrolysis of bis-sulphones or the photoextrusion of sulphur from bis-sulphides. The three-layer paracyclophanes are presented in Scheme 3.

Tetramethyldithiametacyclophane (XXXVII) has been obtained by the cyclisation of bis(3-bromomethyl-2-methyl)-benzophenone with bis(3-mercaptomethyl-2-methylphenyl)-methane in 80% yield[121]:



(XXXVII)

Sulphur-containing anthraceno- and anthraquinononophanes and pentaphenyleno-phanes have been described[132–135]. Dithiadibenzanthracenophane (XL) has been obtained by the reaction of bis(bromomethyl)dibenzanthracene (XXXVIII) with bis(mercaptomethyl)dibenzanthracene (XXXIX) (yield 55%):[139]

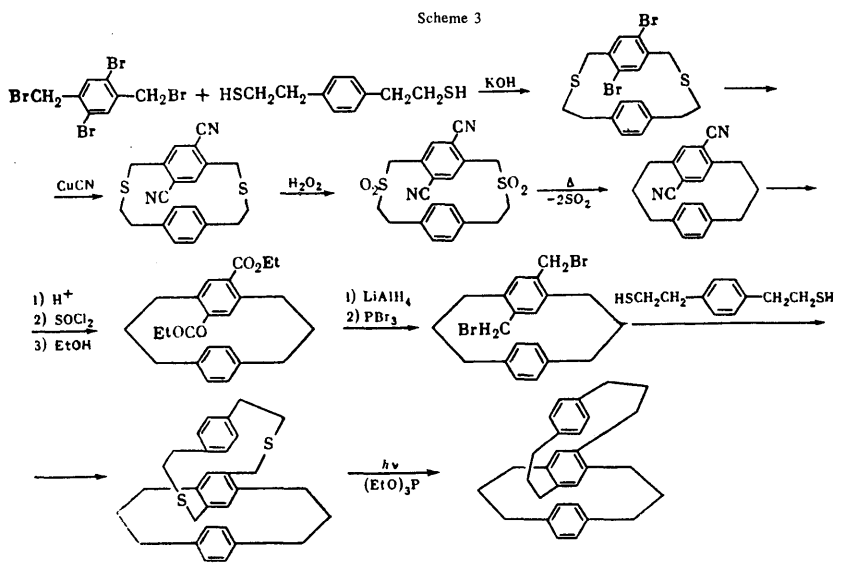


(XXXVIII) X = Br;
(XXXIX) X = SH (XL)

2. Thiophenophanes

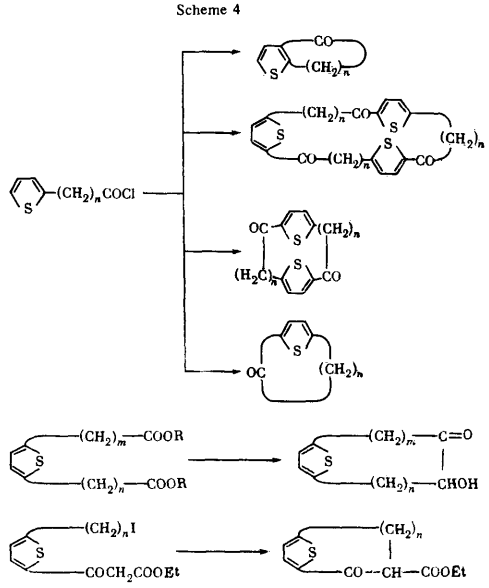
A method based on the intramolecular and intermolecular acylation of the chlorides of ω-thienylalkanecarboxylic acid, the acyloin condensation of 2,5-bis(alkoxycarbonylalkyl)-thiophens, and the intramolecular alkylation of ω-halogenoalkyl-substituted β-ketoesters of the thiophen series have

Scheme 3



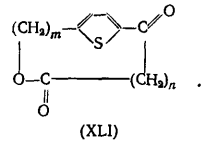
been developed for the synthesis of macrocyclic compounds incorporating the thiophen ring[29,140,144,145,150–152,155,156] (Scheme 4).

Scheme 4



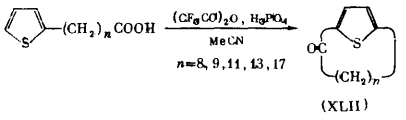
These investigations have been reviewed[35].

The X-ray diffraction determination of the geometrical and conformational parameters of the isomeric *ansa*-ketolactones having the general formula (XLI) and incorporating the thiophen ring[141–143,146–148] made it possible to explain the different ease of formation of macrocyclic ketolactones depending on the position of the ester group in the *ansa*-bridge and also the characteristics of their spectra and physical and chemical properties:



(XLI)

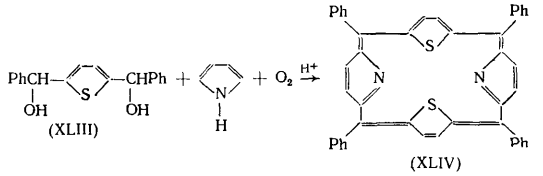
(2,5)-Thiophenophan-1-ones (XLII) have been synthesised by the cyclisation of ω-(2-thienyl)alkanecarboxylic acids in the presence of 85% phosphoric acid and trifluoroacetic anhydride in dry acetonitrile[153,154]:



(XLII)

The yields of the macrocycles (XLII) increase from 9 to 66% with increase of the length of the polymethylene bridge.

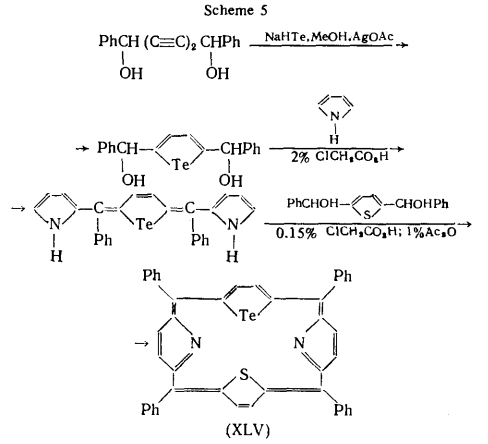
Tetraphenyl-21,23-dithiaporphyrin (XLIV) has been obtained by the reaction of 2,5-bis(α-hydroxybenzyl)thiophen (XLIII) with pyrrole (yield 10%):[157]



(XLIII) (XLIV)

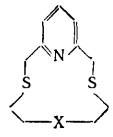
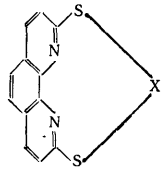
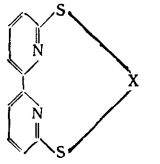
A new tetraphenylporphyrin (XLV), containing sulphur and tellurium atoms together with nitrogen atoms, has been synthesised by the following scheme[185].

Scheme 5



(XLV)

Table 9. Sulphur-containing pyridinophanes.

Compound	X	M.p., °C	Yield, %	Refs.
	S	162—163	50	[158]
	SO	171—174	26	[158]
	SCH_2CH_2S	131—133	38	[158]
	S—S	151—153 *	13	[158]
	N—Me	67—69	11	[158]
	SH_2C—  —CH_2S	213—216 **	19	[158]
	$CH_2CH_2SCH_2CH_2$	263	—	[160]
	$CH_2CH_2OCH_2CH_2OCH_2CH_2$	197	—	[160]
	$CH_2CH_2SCH_2CH_2SCH_2CH_2$	173	—	[160]
	$CH_2CH_2(OCH_2CH_2)_3$	127	—	[160]
	$(CH_2)_6$	156	—	[160]
	$(CH_2)_8$	125	—	[160]
	H_2C—C_6H_4—CH_2	210	—	[160]
		281	—	[160]
	$(CH_2)_8$	71	—	[160]
	$CH_2CH_2(OCH_2CH_2)_3$	205	—	[160]

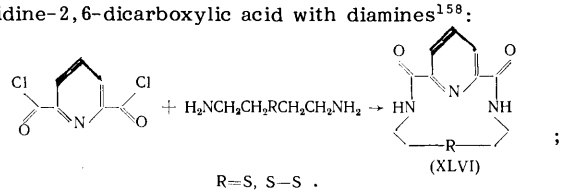
*Sublimation.

**Decomposition temperature.

3. Sulphur-Containing Pyridinophanes

Pyridinophanes have been synthesised by the reaction of 2,6-bis(bromomethyl)pyridine with various α,ω-dithiols (Table 9). The pyridinophanes (XLVI) containing diamide

groups have been obtained by the reaction of the dichloride of pyridine-2,6-dicarboxylic acid with diamines[158]:



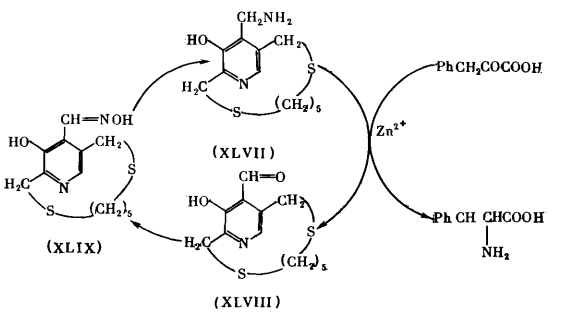
(XLVI)

R=S, S—S .

The sulphur-containing pyridinophanes synthesised form crystalline complexes with the transition metal ions Ag^+, Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, Pd^{2+}, Au^{3+}, and Pt^{4+} (yields 39–96%).

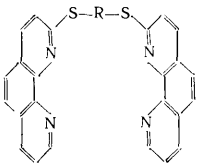
(−)-15-Aminomethyl-14-hydroxy-2,8-dithia[9](2,5)-pyridinophane (XLVII) has been used as a transaminating agent in the reaction with phenylpyruvic acid[115,159]. Zinc salts have been used as catalysts. Pyridoxamine (XLVII) has been obtained from the pyridinophane (XLVIII) by treatment with NH_2OH–HCl–AcOna–EtOH and subsequent reduction of the oxime (XLIV) with $NaBH_2S_3$ in THF. The transamination reaction is carried out by stirring a mixture of the pyridinophane (XLVII), sodium phenylpyruvate, and $ZnClO_4$. $.6H_2O$ at room temperature for 20 h in acetonitrile (Scheme 6); the maximum yield of phenylalanine is 83%:

Scheme 6

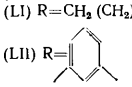


(XLVII) (XLIX) (XLVIII)

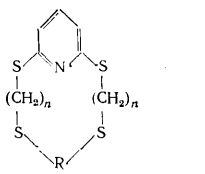
Macroheterocyclic phenanthrolines and dipyrinide (Table 9), in which the bridging sulphur atoms are linked directly to the pyridine ring, have been synthesised by the reaction of 2,9-dichloro-1,10-phenanthroline and 6,6′-dichloro-2,2-bipyridyl with α,ω-dithiolates in 3-methyl-1-butanol[160]. These macroheterocycles do not form crystalline complexes with alkali metal or alkaline earth metal ions, while among heavy metal ions complexes are formed only with silver and mercury ions. The open-chain ligands (L)–(LII) used for comparison readily form complexes with Co^{2+}. It has been suggested that the weak coordinating capacity of the macroheterocyclic ligand synthesised is associated with the shielding effect of the bridging chains[160].



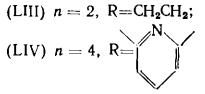
(L) R=$CH_2CH_2XCH_2CH_2$ (X=O, S);
(LI) R=$CH_2(CH_2)_nCH_2$ (n = 3, 4, 9);



(LII) R=



(LIII) n = 2, R=CH_2CH_2;

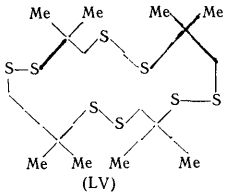


(LIV) n = 4, R=

The pyridinophanes (LIII) and (LIV) have been obtained by the reaction of 2,6-dihalogenopyridines with α,ω-dithiols[161].

IV. MACROHETEROCYCLIC DI- AND POLY-SULPHIDES

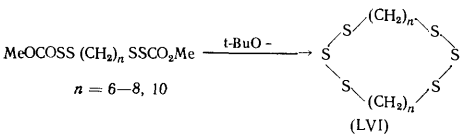
The synthesis of the 16-membered polydisulphide (LV) by treating the isobutene–sulphur monochloride adduct with a solution of sodium hydrogen sulphide has been described[162].



(LV)

The same substance is formed by the reaction of 2-chloro-2-methylpropyl disulphide, methylallyl disulphide, or sodium methylallyl thiosulphate with sodium hydrogen sulphide; the maximum yield of compound (LV) is 45%.

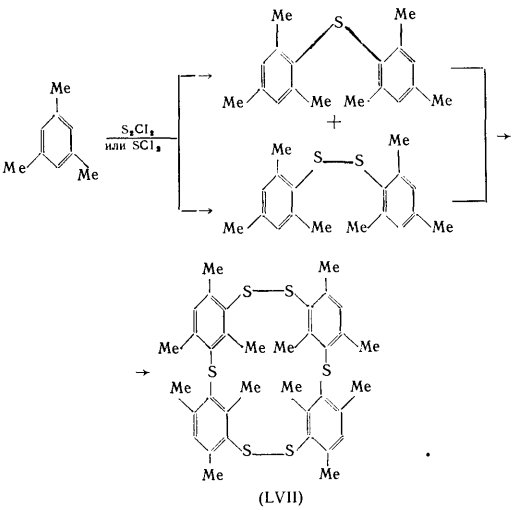
Macroheterocyclic trisulphides have also been formed as a result of the decomposition of polymethylenebis-sulphenyl thiocarbonates by alkoxides[163]:



(LVI)

The yields of the trisulphides (LVI) increases with increase of the length of the bis-sulphenyl thiocarbonate chain. Thus the yields are 16, 22, 50, and 86% respectively for n = 6, 7, 8, and 10.

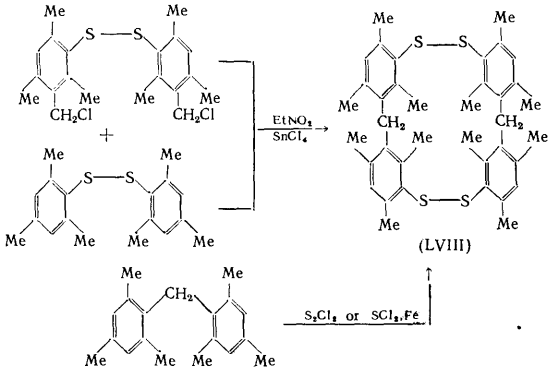
The synthesis of the polythiamacroheterocycle (LVII) has been achieved by the direct introduction of sulphur into mesitylene with the aid of sulphur monochloride or dichloride[164]:



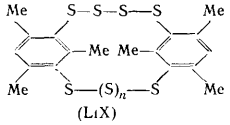
(LVII)

The reaction takes place when the mixture of the reactants is refluxed in chloroform in the presence of iron powder. When sulphur monochloride is used, the yield of compound (LVII) reaches 18%, while in the reaction with sulphur dichloride it does not exceed 3%. The interaction of dimesitylmethane with sulphur monochloride has been studied under analogous conditions and tetrathia[2,1,2,1]metacyclophane (LVIII) with alternating disulphide and methylene linkages

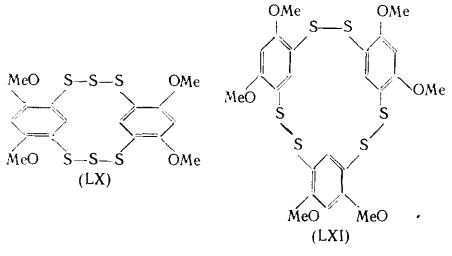
was isolated (yield 15%); in the reaction with sulphur dichloride, compound (LVIII) is formed in 3% yield[165]:



The formation of asymmetric macroheterocyclic polysulphides (LIX) in the reaction of mesitylene-2,4-dithiol with sulphur chlorides was entirely unexpected[166]. Their structure was confirmed by X-ray diffraction and NMR measurements:

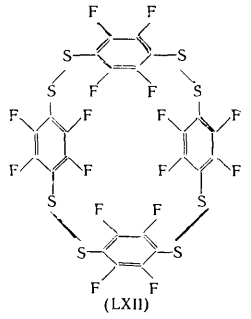


The interaction of 1,3-dimethoxybenzene with sulphur chlorides, catalysed by iron, has been studied at normal dilution and using a high dilution technique[167–169]. In the former case, linear polysulphides were obtained, while under the conditions of high dilution a mixture of two macroheterocycles, (LX) and (LXI), is formed in yields of 6 and 1.5% respectively:



One of the methods of synthesis of macroheterocyclic polysulphides involves the oxidation of dithiols. It was stated previously that the oxidation of benzene-1,4-dithiols leads to the formation of polymeric disulphides[170–172]. However, macroheterocyclic compounds have been synthesised on treatment with iodine at high dilution in 30% yield[173]. The oxidation of naphthalene-1,4-dithiol in the presence of alkali metal hexacyanoferrates(III) also leads to a macroheterocyclic compound[174].

The oxidation of tetrafluorobenzene-1,4-dithiol in diphenyl sulphoxide yielded the macroheterocyclic tetrakisdisulphide (LXII) in 95% yield[175]. The ease of conversion of tetrafluorobenzene-1,4-dithiol into the macrocyclic polysulphide (LXII) is unique. On the other hand, when an attempt was made to oxidise benzene-1,4-diothiol, 2,5-dimethoxybenzene-1,4-dithiol, and tetramethylbenzene-1,4-dithiol under analogous conditions, only polymeric products were isolated. The oxidation of tetrachlorobenzene-1,4-dithiol has been investigated but the molecular weight of the entire product synthesised could not be determined owing to its low volatility and solubility[175].

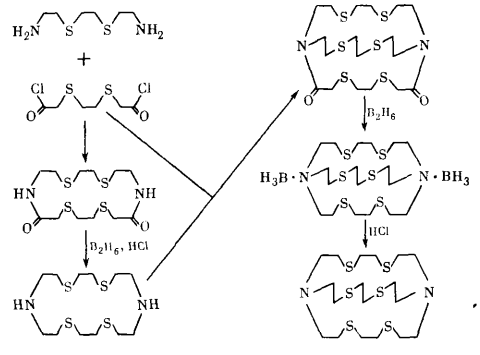


V. MACROHETEROBICYCLIC AND MACROHETEROTRICYCLIC SULPHIDES

In 1969 Dietrich et al.[176,177] synthesised a series of macrobicyclic polyaminoethers which have been called cryptands. The main characteristic of compounds of this type is the stability of their complexes with a wide range of cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, etc.). Cryptates—the complexes of macrobicyclic polyaminoethers—are readily soluble in water and organic media and their stability is superior to that of the complexes with macromonocyclic polyaminoethers.

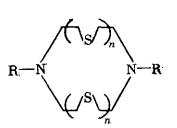
Sulphur-containing cryptands have been obtained in the following way (Scheme 7).[178] The corresponding dichlorides of oxa- or thia-dicarboxylic acids were condensed with 1,8-diamino-3,6-dithiaoctane at high dilution. The diamides isolated were reduced with diborane and, after hydrolysis with hydrochloric acid, were converted into monocyclic diamines. The latter were again condensed with dicarboxylic acid dichlorides and the bicyclic diamides formed were converted, like the monocyclic compounds, into macrobicyclic sulphur-containing polyaminoethers (Scheme 7):

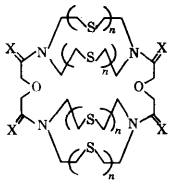
Scheme 7

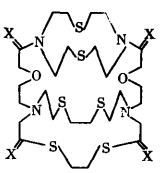


Macropolycyclic ligands can form polynuclear cryptates by incorporating two or more metal cations in the inner cavity within the molecule. Such systems are at present of great interest as models of polynuclear biological complexes and also as polynuclear catalysts. A general synthetic method has been developed[183,184] for the construction of cylindrical macrotricyclic systems which contain rings with different numbers of heteroatoms and different sizes of the inner cavity and a study has been made of their complex formation reactions with univalent and bivalent copper salts.

The sulphur-containing tetra-amide (LXX) has been synthesised by condensing the macroheterocycle (LXVI), containing reactive substituents at the nitrogen atoms, with the macroheterocycle (LXIII). Subsequent reduction of the tetra-amide (LXX) with diborane leads to the formation of the cylindrical macrotricyclic polythiatetra-amine (LXXI). The sulphur-containing macrotricyclic compounds (LXXII) to (LXXV) have been obtained analogously[183,184].





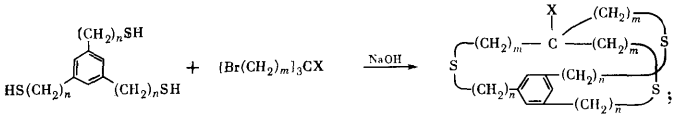


(LXIII): $n=1$, R = H;
(LXIV): $n=1$, R = Me;
(LXV): $n=1$, R = $COCH_2OCH_2COOH$;
(LXVI): $n=1$, R = $COCH_2OCH_2COOC_6H_4NO_2$-*n*;
(LXVII): $n=2$, R = Me;
(LXVIII): $n=2$, R = $COCH_2OCH_2COOH$;
(LXIX): $n=2$, R = $COCH_2OCH_2COOC_6H_4NO_2$-*n*

(LXX): $n=1$, X = O;
(LXXI): $n=1$, X = H_2;
(LXXII): $n=2$, X = O;
(LXXIII): $n=2$, X = H_2

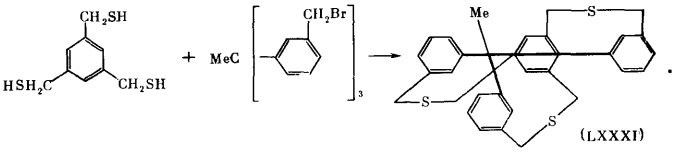
(LXXIV): X = O;
(LXXV): X = H_2

A single-stage method of synthesis of macrobicyclic sulphides[179] has been developed. The macrobicyclic compounds (LXXVI)–(LXXX) have been obtained by the reaction of 1,3,5-tris(mercaptomethyl)- or 1,3,5-tris(mercaptoethyl)-benzene with tris(bromoalkyl)methane or tris(bromoalkyl)-ethane in the presence of sodium hydroxide:



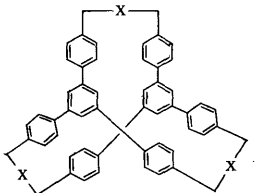
(LXXVI): $n=1$, $m=3$, X = H;
(LXXVII): $n=1$, $m=2$, X = H;
(LXXVIII): $n=2$, $m=3$, X = H;
(LXXIX): $n=2$, $m=2$, X = H;
(LXXX): $n=2$, $m=1$, X = Me.

1,3,5-Tris(mercaptomethyl)benzene has also been used to synthesise the symmetrical triply bridged [2,2,2]cyclophane (LXXXI):[180]

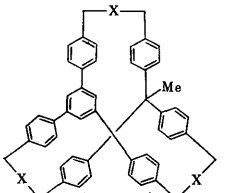


(LXXXI)

The triply bridged polythiacyclophanes (LXXXII)–(LXXXV) have also been synthesised[181]. Trithiatriphenylbenzophane has been produced by the reaction of 1,3,5-tris[(*p*-mercaptomethyl)phenyl]benzene with 1,3,5-tris[(*p*-bromomethyl)-phenyl]benzene in 31% yield:

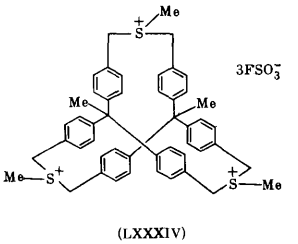


(LXXXII)
X = S, SO_2, $\overset{+}{S}Me \cdot \bar{F}SO_3$

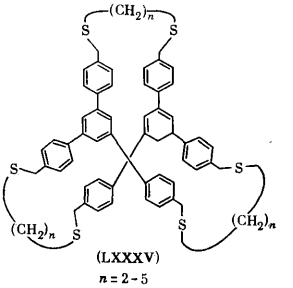


(LXXXIII)
X = SO_2, $\overset{+}{S}Me \cdot \bar{F}SO_3$

Compounds (LXXXV) have been obtained by the reaction of 1,3,5-tris[(*p*-bromomethyl)phenyl]benzene with different α,ω-dithiols:



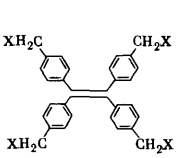
(LXXXIV)



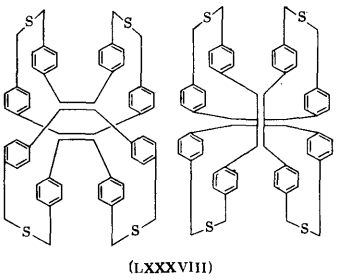
(LXXXV)
$n=2-5$

The reaction of equivalent amounts of the tetrabromo-compounds (LXXXVI) and the tetrathiol (LXXXVII) at high dilution leads to compound (LXXXVIII), with the four-sided bridged tetraphenylene system in the form of a mixture of two stereoisomers with parallel and orthogonal orientations of the central double bond (Scheme 8);[182] the yield of compound (LXXXVIII) is 4%.

Scheme 8



(LXXXVI): X = Br;
(LXXXVII): X = SH



(LXXXVIII)

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Thus analysis of the literature data has shown that the chemistry of sulphur-containing macroheterocycles has been in recent years the subject of increasing attention of investigators. This is due primarily to the possibility of using macroheterocyclic sulphides as complex-forming agents and extractants for heavy metals. New studies in this field will undoubtedly promote their wider practical application.

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Reactivity and Conformation of Systems containing a Three-membered Heterocycle Conjugated with an Unsaturated Group

A.V.Kamernitskii and A.M.Turuta

Steroidal epoxides, aziridines, and episulphides containing a vicinal unsaturated group (ketone or hydrazone) are used as examples to examine, systematise, and generalise reactions involving nucleophilic opening of a three-membered ring. The influence of an adjacent substituent on the structural and stereochemical trends of such reactions is discussed. A list of 107 references is included.

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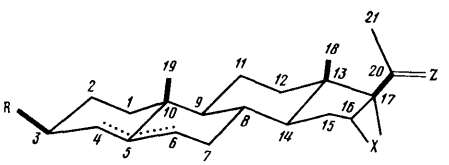
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I. INTRODUCTION

The many reviews covering epoxides[1-5], aziridines[6,7], and episulphides[8,9] devote only insignificant space to the reactions of three-membered heterocycles conjugated with keto or other unsaturated group[1,7]. Often the general principles of the chemistry of three-membered rings cannot be used to foretell the direction of ring-opening in such systems, and it is difficult to predict and explain the results of reactions in any particular case[10]. Even in the relatively well-studied field of keto-epoxides definite correlations have not been established between substrate structure, reagent, and the conditions and direction of reactions: several views are held on the mechanism which best describes such reactions[3,10,11]. It may be supposed *a priori* that the direction of ring-opening will be determined by the concerted (or competing) influence of the nature of the heterocycle, the adjacent unsaturated group, and their relative arrangement (interaction). However, to determine the role of each of these factors in studying conformationally labile systems such as aliphatic epoxy(or epi-imino)-ketones is an almost hopeless task.

In fact the nature of the electronic interactions between three-membered ring (epoxy, epi-imino, cyclopropyl)† and neighbouring carbonyl group is usually described as conjugation resulting from orbital overlap of banana bonds of the ring and a *p*-orbital of the carbonyl group[12-14]. After Walsh had predicted[13] the geometrical requirements for such interaction, Cromwell[12] showed that maximum conjugation in such systems is achieved with the planes of carbonyl group and three-membered ring parallel and the keto-group on a bisector of the ring. Therefore the problem of reactivity and direction of ring-opening must, of course, be considered in connection with the conformation of the adjacent portion of the molecule.

The present Review represents an attempt to systematise scission reactions of three-membered rings with steroids as conformationally rigid models, in which the side-chain containing the unsaturated group adjacent to the three-membered ring is capable of rotating about the $C_{(17)}-C_{(20)}$ bond:



β-region (front) of molecule

X=O, NH, NAc, S Z=O, $NNHCO_2C_2H_5$ R=OH, OAc, Δ^5; O, Δ^4

α-region (rear) of molecule

Because of structural and electronic features, however, the barrier to rotation is quite high, and the molecule is fixed in one of the preferred conformations depending on the nature of the heterocycle and its immediate environment[15-17]. This enables the relative influence of the above factors on reactivity and direction of reaction to be traced from stereochemically reliable data on ring-opening in such systems.

II. RING-OPENING IN EPIMERIC 16,17-EPOXY-20-OXO-STEROIDS

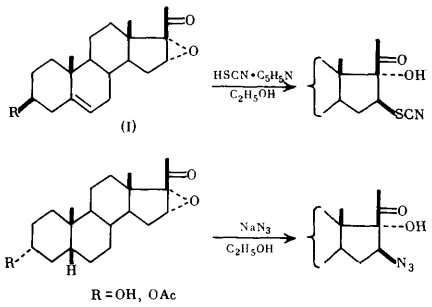
Among the 16,17-hetero-substituted 20-keto-steroids discussed only the epoxy-ketones have been widely studied; they showed clearly that the structural and stereochemical direction of ring-opening depends on the structure of the oxide, the nature of the reagent, and the reaction conditions. Most of the reactions studied are examples of acid-catalysed nucleophilic ring-opening. Exceptions are provided by the scission of 16,17-epoxy-20-ketones by highly nucleophilic reagents and by their aminolysis, which we shall consider first. In the former case solvation of the oxide ring by protons of the solvent provides electrophilic assistance to scission, and in the latter case the reagent itself acts as an alkaline catalyst.

1. Ring-opening under Neutral Conditions and Aminolysis

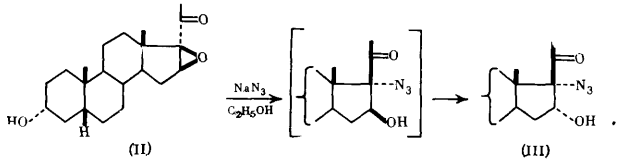
In neutral media 16,17α-epoxy-20-oxo-steroids (I) undergo exclusively *trans*-opening of the oxide ring at the more

†Episulphides containing a vicinal unsaturated group have not hitherto been studied.

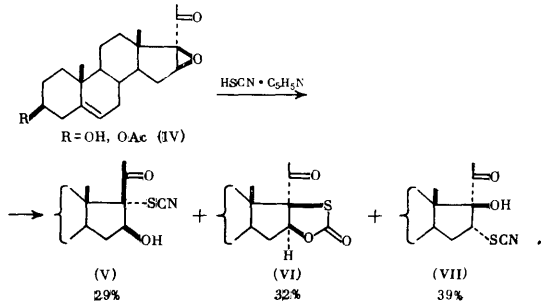
substituted carbon atom[18-20]:



A protic solvent undoubtedly helps to increase the reaction velocity, for in an aprotic medium the reaction, e.g. with thiocyanic acid, does not take place[19]. The analogous reactions of 16,17β-epoxy-20-oxo-steroids occur with the opposite structural selectivity. The only product of azidolysis of the 16,17β-epoxide (II) under identical conditions is that of attack by the azide ion at the tertiary atom with Walden inversion, epimerisation at the $C_{(16)}$ atom being regarded[20] as a secondary process:



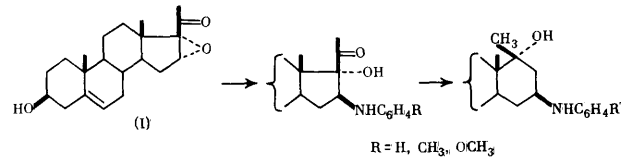
Reaction of the 16,17β-epoxide (IV) with thiocyanic acid is not so selective[21,22]. The tendency to preferential but not exclusive attack at the tertiary centre is maintained. However, both *trans*- and *cis*-scission products (V) and (VI) are formed, with a total yield of 60–65%:[21]



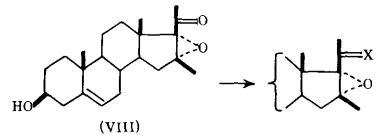
Attack at the secondary atom with formation of the *trans*-hydroxy-thiocyanate (VII) takes place to a lesser but appreciable extent (~40%).

These results on the scission of 16,17β-epoxy-20-oxo-steroids by thiocyanic and hydrazoic acids, at first glance contradictory, become consistent on the assumption that formation of the 17α-azide (III) is a consequence of a retroaldol type of epimerisation[23] not of one, as had been assumed[20], but of two 17-azides, with α- and β-configurations of the azide function, formed in the reaction medium. Such epimerisation is, of course, completed by stabilisation of the thermodynamically more stable isomer (III) having β-orientation of the 17-acetyl group.

No information has been published on the aminolysis of 16,17β-epoxy-20-oxo-steroids, while results on the structure and configuration of products obtained with ring-opening of their 16,17α-epimers by amines are very few and contradictory[24]. A critical approach must be adopted to most of the early literature, mainly patents, with reference to the formation of 16-amino-17α-hydroxy-20-oxo-steroids on reaction with primary and secondary amines[25-27], since structures were assigned to the products without evidence. According to Frangulyan et al.[24,28,29] opening of the oxide ring of 16,17α-epoxy-20-oxo-steroids by aromatic amines (aniline, *p*-toluidine, *p*-anisidine) takes place with D-homoisomerisation, which implies initial formation of 16β-amino-17α-hydroxypregnanes, attempts to isolate which proved unsuccessful:



Even these few results show that, in the ring-opening of 16,17α-epoxy-ketones by bases, attack by the nucleophile is directed at the secondary centre, the β-position. When such attack is sterically hindered, as e.g. in the action of ammonia or a primary amine on the 16,17α-epoxy-16β-methyl-ketone (VIII), reaction takes place at the 20-oxo-group with elimination of water and without involving the oxide ring[30]:

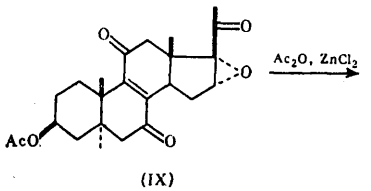


2. Acid-catalysed Ring-opening of Epimeric 16,17-Epoxy-20-oxo-steroids

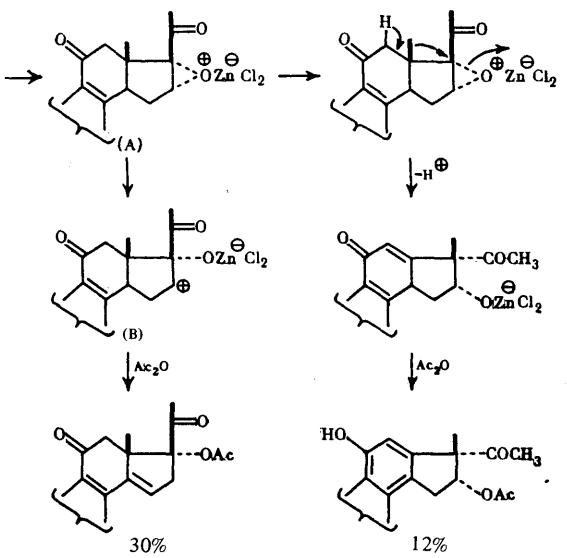
Reactions of this type include the ring-opening of 16,17-epoxy-20-oxo-steroids by hydrohalic acids (below) and the addition of water, acetic acid, methanol, thioacetic acid, hydrazoic acid, and other reagents catalysed by mineral or Lewis acids. They have been referred to many times in the literature, but with few exceptions the complete pattern of structural and steric trends has not been studied. The present Review is confined to published results, including a complete analysis of the reaction mixture. Protonation of the oxide ring or coordination with a Lewis acid is a necessary stage in these processes[3]. The direction of opening of the oxide ring depends both on the structure and stereochemistry of the initial oxide and on the nucleophilicity of the reagent.

In the acid-catalysed ring-opening of 16,17α-epoxy-20-oxo-steroids the tendency of the oxide to break at the tertiary centre closest to the keto-group increases in proportion to the decrease in nucleophilicity of the reagent. Incorporation of the nucleophile at the $C_{(17)}$ atom is observed only in exceptional cases and to an extremely insignificant extent. Stabilisation of the positive centre formed is usually completed by 1,2-migration of the angular methyl group. Thus in reactions of this type with weak nucleophiles or in their absence intermediate products are stabilised by rearrangements involving rupture mainly of the $C_{(17)}$–O and to a less extent the $C_{(16)}$–O bond[31], with the quantity of open-chain products apparently measuring the stability of the intermediates. A reaction of interest from

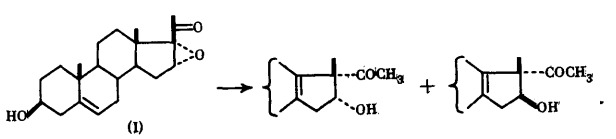
this point of view is that of the 16,17α-epoxide (IX) with acetic anhydride catalysed by zinc chloride[32], regarded as taking place by two competing routes, one of which involves a Wagner–Meerwein rearrangement by a synchronous mechanism with elimination of a proton from $C_{(12)}$ followed by enolisation and replacement of zinc chloride by an acylium ion:



(IX)

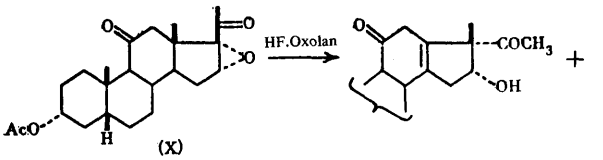


The alternative ring-opening of the intermediate A will give the 16-carbocation B, which is stabilised with elimination of a proton from the $C_{(15)}$ atom followed by allyl rearrangement of the $\Delta^{15,16}$ bond to a conjugated position. Apparently the relative contents of products formed with rupture of the $C_{(17)}$–O or $C_{(16)}$–O bond in reactions of this type depend to a considerable extent on the structure of the initial oxide and the catalyst used. Thus hydrolysis of the 16,17α-epoxide (I) in methanol catalysed by perchloric or sulphuric acid is 75–80% accompanied by a Wagner–Meerwein rearrangement with formation of an equilibrium mixture of epimers at the $C_{(16)}$ atom[33]:

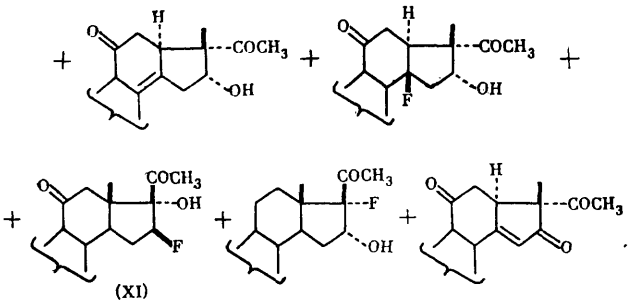


(I)

A similar structural trend is exhibited by the action of hydrogen fluoride on the epoxide (X), which differs from the reactions with hydriodic and hydrobromic acids[34–36] in involving rupture of the $C_{(17)}$–O bond and is usually completed by migration of the angular methyl group[37]; the expected *trans*-fluorohydrin (XI) is formed in only 2% yield:



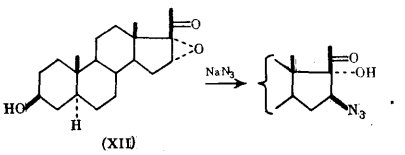
(X)



(XI)

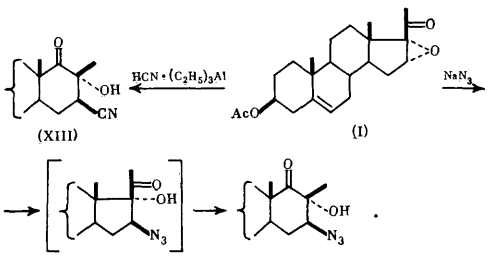
Ring-opening of 16,17α-epoxy-ketones with hydrobromic or hydriodic acid, which is most widely used in practice, is reported as yielding 30–70% of *trans*-products with rupture of the $C_{(16)}$–O bond and incorporation of the halogen at this position[34–36].

The acid-catalysed reactions of 16,17α-epoxy-20-oxo-steroids with such strongly nucleophilic reagents as e.g. azide and cyanide ions exhibit high stereo- and regio-selectivity. The course of the reaction of the epoxide (XII) with sodium azide in dimethyl sulphoxide (DMSO) catalysed by sulphuric acid is identical[38] with that described above in ethanol:



(XII)

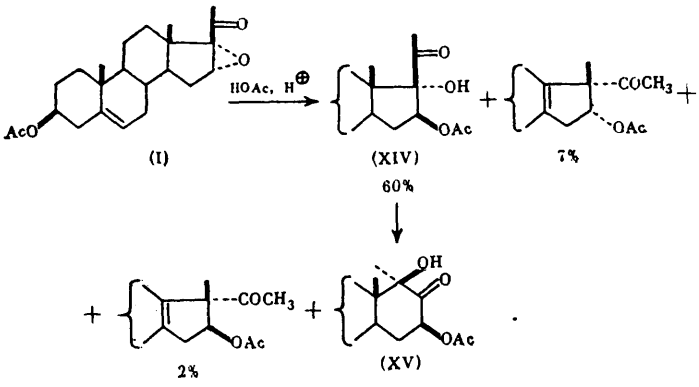
The same reaction is reproduced under identical conditions by the epoxide (I),[39] but a D-homostructure is attributed to the final product. It must be assumed that the absence of D-homoisomerisation in the preceding case is due to the greater stability of the D-ring in 5α-steroids. A similar result has been reported for scission of epoxide (I) by the hydrogen cyanide–triethylaluminium complex[40]; formation of the D-homoketone (XIII) is not unexpected, because of the Lewis nature of the reagent:



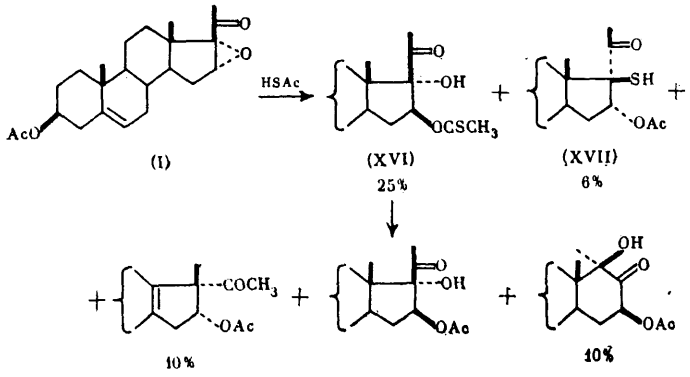
(XIII) (I)

Acetic and thioacetic acids, which are quite strong nucleophiles but considerably weaker than hydrazoic, thiocyanic, hydrobromic, and hydriodic acids, react with the oxide ring

of 16,17α-epoxy-20-oxo-steroids only in the presence of a mineral acid as catalyst. Such reactions are characterised not only by preferential *trans*-opening of the oxide at the secondary centre but also by rupture of the $C_{(17)}$–O bond[41,42]. The main direction in which 16,17α-epoxides are opened by acetic acid is *trans*-attack at the $C_{(16)}$ atom with formation of the 16β-acetate (XIV), which apparently isomerises into the D-homoketone (XV):[41]



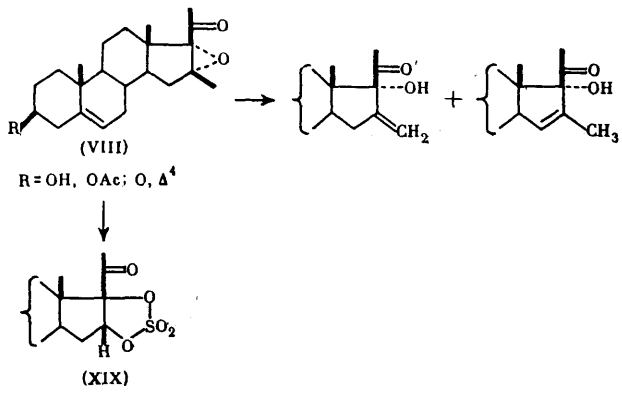
Rupture of the $C_{(17)}$–O bond followed by a Wagner–Meerwein rearrangement is observed to a considerably less extent. Such is the general direction in which the oxide (I) reacts with thioacetic acid in the presence of an inhibitor of free-radical addition and sulphuric acid as catalyst[42]. Thioacetic acid, which reacts in the *O*-form, attacks the $C_{(16)}$ atom to form the 16-O-thioacetate (XVI), which under the reaction conditions hydrolyses to the diacetate (XVIII):



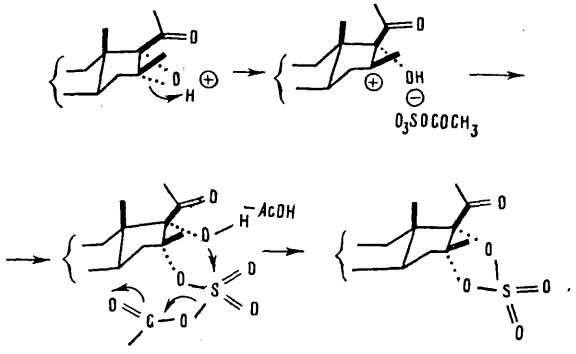
A feature of the reaction is formation of the 17β-thiol (XVII), formally a product of *trans*-opening of the oxide by hydrogen sulphide with attack at the tertiary carbon atom. It must not be forgotten, however, that hydrogen sulphide ions are able to add to a carbonyl group[3,43], so that an alternative possibility is addition to the keto-group of hydrogen sulphide formed by decomposition of thioacetic acid, followed by intramolecular attack at the $C_{(17)}$ atom.

In the ring-opening of 16,17α-epoxy-16β-methyl-20-oxo-steroids by acidic reagents, in contrast to desmethyl oxides, incorporation of the nucleophilic reagent is not usually observed: reactions are completed by formation of unsaturated alcohols, the proportions of which vary with the reaction conditions (reagent, solvent), their formation being regarded as resulting from stabilisation of the $C_{(16)}$ carbocation by elimination of one of the neighbouring protons[44,45]. The direction of stabilisation is largely determined by the possibility of solvation of the 16-centre.

An extremely interesting reaction is the production of 16α,17α-cyclosulphates (XIX) in the ring-opening of the 16β-methyl oxide (VIII) by oleum in glacial acetic acid or by a mixture of acetic anhydride and sulphuric acid in acetic acid, formally involving *cis*-opening of the oxide ring and addition of sulphur trioxide[46]:



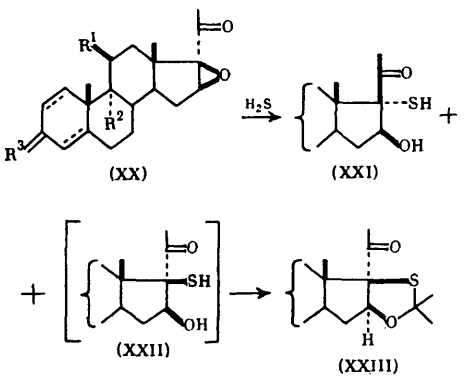
The postulated mechanism involves rupture of the $C_{(16)}$–O bond in the protonated form of the oxide by acetylsulphuric acid, apparently formed by interaction of acetic anhydride with sulphuric acid. Because of steric hindrance by the 13-methyl group, approach of the acetylsulphate ion to the $C_{(16)}$ atom takes place preferentially from the rear of the molecule:



Intramolecular acylation of the free hydroxy-group of the mixed anhydride of sulphuric and acetic acids is assumed to take place in the intermediate product, with formation of a cyclic sulphate[44]. The ease of such transesterification is explained by the close approach of the vicinal *cis*-substituents in the five-membered ring, and bears an analogy to the well-known 17 → 16 acyl migration[1].

The structural direction of ring-opening in 16,17β-epoxy-ketones is less influenced by the reaction conditions: all the reported acid-catalysed reactions occur regiospecifically with rupture of the carbon–oxygen bond at the tertiary carbon atom closest to the carbonyl group. The subsequent behaviour of the resulting intermediate, however, depends to a considerable extent on the conditions: use of an acid catalyst and weakening of the nucleophilicity of the reagent favour isomerisation involving the $C_{(17)}$ centre. On interaction with strongly nucleophilic reagents such as hydrazoic acid[20,38,47], hydrobromic acid[48,49], and hydrogen sulphide[22,50] stabilisation of this centre is effected solely by addition of the nucleophilic species. *trans*-Opening of the oxide at the $C_{(17)}$ atom with incorporation of the nucleophile from the

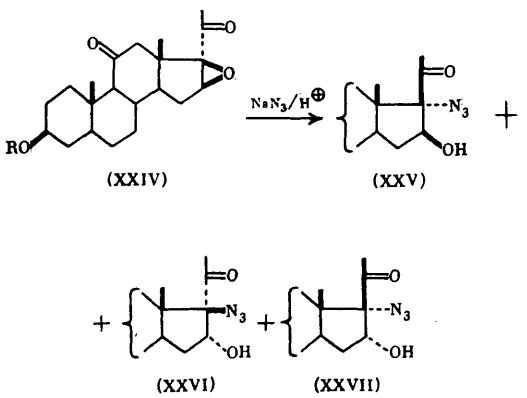
rear of the molecule is the preferred but not exclusive direction of the reactions of 16,17β-epoxy-ketones, for which addition of the nucleophile at the $C_{(17)}$ atom from the β-region is also very characteristic. The stereochemistry of opening of the epoxide ring in (XX) with hydrogen sulphide and sodium azide is interesting. In the reaction of the epoxide with hydrogen sulphide in acetic acid catalysed by toluene-*p*-sulphonic acid the preferred product of *trans*-opening—the thiol (XXI)—is accompanied[22,50] by the *cis*-16,17β-isomer (XXII), identified as the acetonide (XXIII):



(XX) (XXI) (XXII) (XXIII)

R^1=H, OH, OAc;
R^2=H, F;
R^3=O, β-OAc, $\Delta^{1,4}$, Δ^4, Δ^5.

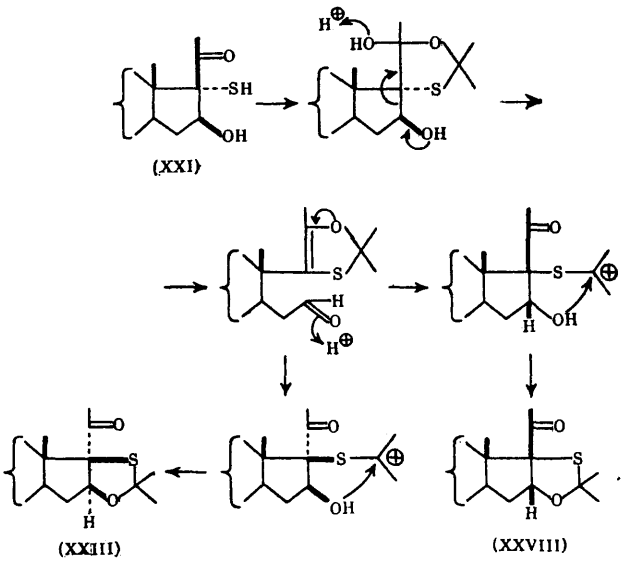
Reaction of the epoxide (XXIV) with sodium azide in the presence of sulphuric acid in DMSO involves formation of the three epimeric azides (XXV)–(XXVII), the proportion of the 16,17α-isomer (XXVII) increasing with the duration of reaction[38]:



(XXIV) (XXV) (XXVI) (XXVII)

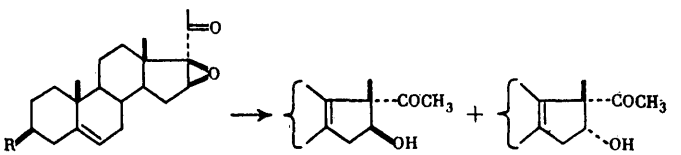
R=H, Ac.

The view[22,37] that a 17α-azido(or mercapto)-16β-ol is formed initially, and isomerises under the reaction conditions by a retroaldol mechanism, is supported by experiment. Thus the *trans*-thiol (XXI) condenses with acetone in the presence of an acid to give the oxathiolan (XXVIII) and its epimer (XXIII), whose formation can be represented



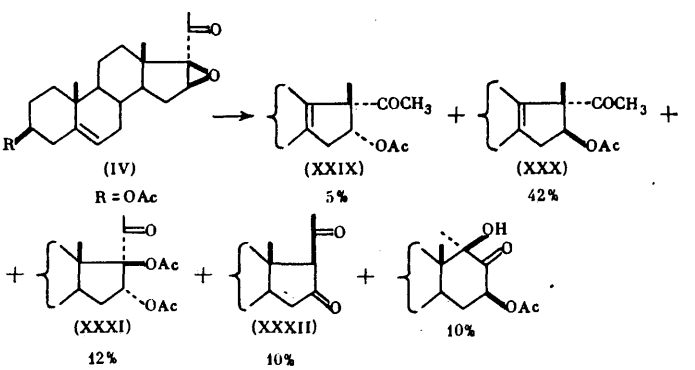
(XXI) (XXIII) (XXVIII)

Nevertheless, these results do not exclude the possibility of direct attack by the hydrogen sulphide or the azide ion from the front of the molecule at the $C_{(17)}$ atom. The tendency for the oxide ring to open at this atom from the β-region in the acid-catalysed reactions of 16,17β-epoxy-20-oxo-steroids is especially clearly evident in the hydrolysis of the epoxide (IV), which occurs solely with migration of the angular methyl group[33]:



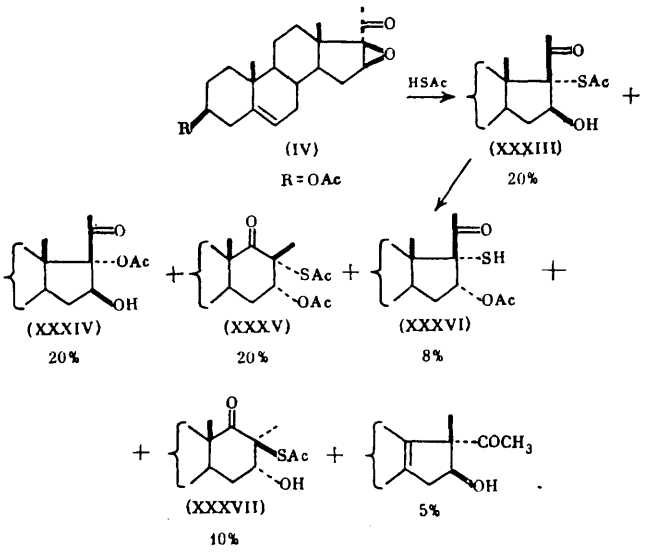
(IV)
R=OH.

Such a structural trend is maintained in the acetolysis of the β-epoxide (IV), when Wagner–Meerwein rearrangement products (XXIX) and (XXX) are accompanied by the *trans*-diacetate (XXXI), formation of this last compound being observed by attacking with the acetate ion from the β-region to neutralise the 17-carbocation and then epimerising and acetylating at $C_{(16)}$:[33]



(IV) (XXIX) (XXX) (XXXI) (XXXII)
R=OAc 5% 42% 12% 10% 10%

The *S*-thioacetate (*O*-thioacetate) ion is more nucleophilic than acetate, which influences the action of thioacetic acid on the β-epoxide (IV), when incorporation of the nucleophile at the $C_{(17)}$ atom from the rear of the molecule is the main route[51,52]. The *cis*-isomer (XXXVI) is a secondary product of epimerisation of the 17α-*S*-thioacetate (XXXIII) formed initially, while the 17α-acetate (XXXIV) is a secondary product of hydrolysis of the 17α-*O*-thioacetate formed in the reaction:

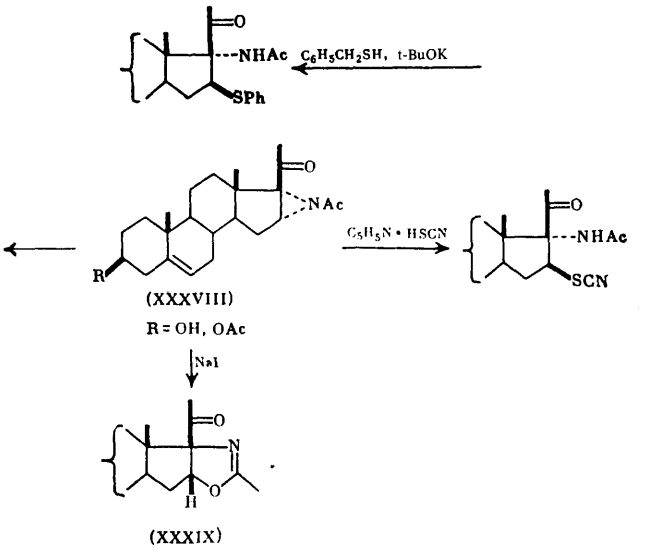


Formation of the D-homoisomers (XXXV) and (XXXVII) is apparently a consequence of D-homoannelation of the primary products of ring-opening.

III. OPENING OF THE AZIRIDINE RING IN 16,17α-EPI-IMINO-20-OXO-STEROIDS AND THEIR *N*-ACETATES

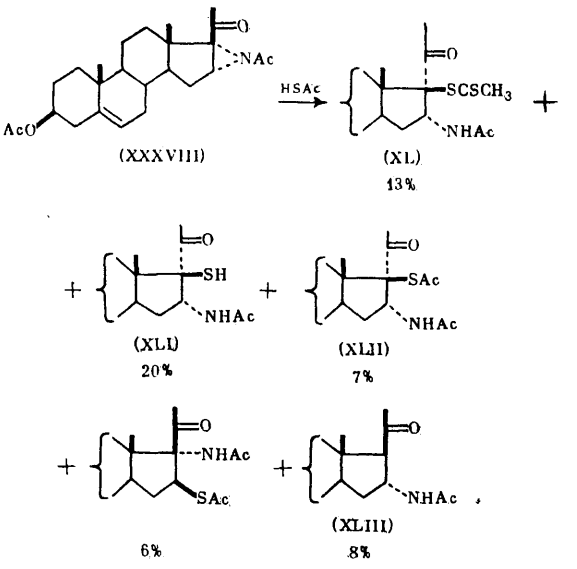
The chemistry of 16,17-epi-imino-20-oxo-steroids has not been developed so actively as that of the 16,17-epoxy-derivatives. Of the two epimeric 16,17ξ-epi-imino-ketones only the 16,17α-isomer has been prepared for study of its ring-opening reactions[53–59]. Existing results indicate firstly low reactivity not only of basic (NH) but also of activated# aziridines in ring-opening and secondly an enhanced tendency for the 20-oxo-group to undergo nucleophilic addition. Thus 16,17α-epi-imino-20-oxo-steroids and their *N*-acetates are inert under conditions under which the corresponding epoxides undergo ring-opening (under the influence of water, hydrazoic acid, acetic acid, methanol), and do not react with potassium thiocyanate in acetic acid[58]; under more severe conditions, in particular catalysis by mineral acids, a Wagner–Meerwein rearrangement takes place exclusively. 16,17α-Acetylepi-imines react only with such nucleophilic reagents as benzenethiol[65,56], pyridine–thiocyanic acid[58], and sodium iodide[57].

These reactions occur by paths characteristic of bio-molecular nucleophilic substitution with rupture solely of the $C_{(16)}$–N bond with inversion of configuration at this centre:



Formation of the 2′-methyl-[16,17α-*d*]oxazoline (XXXIX) by the action of sodium iodide on (XXXVIII) [39] must apparently be regarded as involving double Walden inversion–initial attack by the iodide ion at the $C_{(16)}$ atom followed by intra-molecular substitution of iodine by an internal nucleophile from the rear of the molecule.

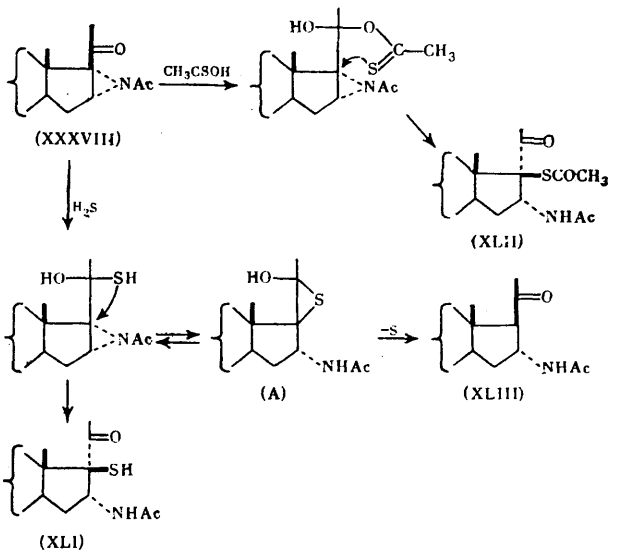
The course of reaction of the *N*-acetylepi-imine (XXXVIII) with thioacetic acid contradicts the general rule of orientation, and leads to preferential rupture of the tertiary $C_{(17)}$–N bond:



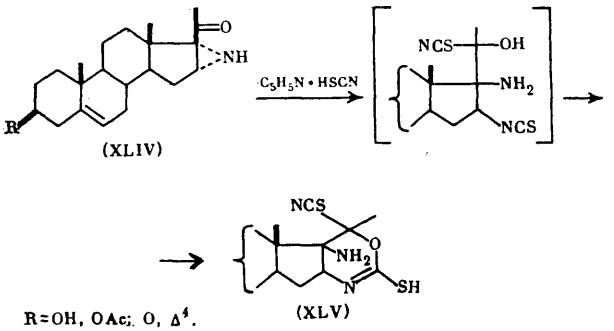
It could be included formally among acid-catalysed reactions of activated aziridines, which take place exclusively (above) with rupture of the $C_{(17)}$–N bond, completed by a Wagner–Meerwein rearrangement. Stabilisation of the $C_{(17)}$ centre should then lead not only to *trans*-addition of the *S*-acetate ion but also to migration of the angular methyl group, which has not been observed. The most acceptable explanation of the observed anomaly[59] is that the largest partial positive charge in the *N*-acetylepi-imine molecule (XXXVIII) is localised on the carbonyl $C_{(20)}$ atom, and this with the

#Activated aziridines have a substituent attached to the nitrogen atom, capable of stabilising the negative charge formed on the nitrogen in the transition state when the compound reacts with a nucleophile[6].

general inertness of the molecule creates favourable conditions for nucleophilic attack on this centre, the reactive species being thioacetatic either *S*- or *O*-acid:

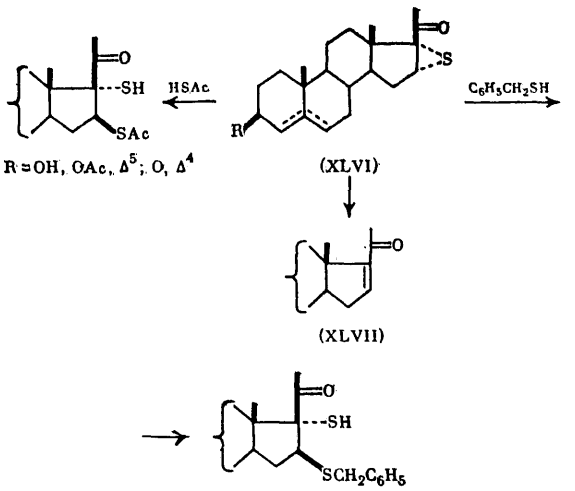


Subsequent intramolecular attack on the $C_{(17)}$ atom with synchronous rupture of the $C_{(17)}$–N bond is assumed to yield the amides (XLI) and (XLII), the former being acylated under the reaction conditions by thioacetic *O*-acid to give (XL). In terms of this scheme formation of the amide (XLIII) was regarded as involving the intermediate episulphide (A), which is desulphurised under acid conditions. This mechanism is consistent with the above tendency of hydrogen sulphide to add to the carbonyl group in epoxy-ketones[3] and also with that of thiocyanic acid to attack the keto-group in 16,17α-epi-imines (XLIV) to form (XLV) [60]



IV. REACTIVITY AND DIRECTION OF RING-OPENING IN 16,17α-EPITHIO-20-OXO-STEROIDS

Epithio-ketones as a class have remained almost unstudied, and no data on physicochemical properties or chemical behaviour are available other than those obtained for 16,17α-epithio-keto-steroids obtained in the Reviewers' laboratory[61,62]. 16,17α-Episulphides are intermediate in reactivity[22,61] between the corresponding oxygen and nitrogen compounds. They are inert under conditions under which the corresponding 16,17α-epoxides undergo ring-opening by such reagents as acetic, thiocyanic, and hydrazoic acids and methanol[62]. Raising the temperature or increasing the duration of reaction leads to elimination of sulphur with formation of the enone (XLVII) and subsequent addition of the nucleophilic reagent to the resulting double bond:



An exception is provided by the reactions of the episulphide (XLVI) with thioacetic acid and with phenylmethanethiol, which involve *trans*-opening of the ring at the less substituted atom $C_{(16)}$. Nucleophilic desulphurisation of the episulphide (XLVI) competes with nucleophilic ring-opening and in most cases predominates. Several aspects must be noted: (*a*) catalysis by a mineral acid (hence protonation of the episulphide ring) is not a necessary condition for elimination reactions [in a weak nucleophile—methanol, acetic acid—the epithio-ketone (XLVI) is stable in the presence of a mineral acid at 20 °C]; (*b*) the presence in the reaction medium of a strong nucleophile promotes desulphurisation even in the absence of a mineral acid (potassium thiocyanate in ethanol at ~80 °C); and (*c*) desulphurisation is equally promoted by a base. In contrast to epoxy(and epi-imino)-ketones the isomeric epithio-ketones (XLVI) apparently do not undergo reactions involving rupture of the $C_{(17)}$–S bond with stabilisation of the resulting electrophilic centre by 1,2-migration of the angular methyl group. If this bond is broken, the molecule is most probably stabilised by elimination of sulphur.

V. INVOLVEMENT OF A HYDRAZONE GROUP IN RING-OPENING IN 16,17-EPOXY(EPI-IMINO, EPITHIO)-20-OXO-STEROIDS

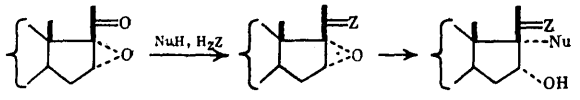
Replacing a keto-group by a hydrazone fragment increases markedly the reactivity of α-substituted ketones in elimination and substitution reactions, in which configuration is usually maintained[63]. This property of hydrazones has been thoroughly studied from both practical and theoretical points of view in a series of investigations undertaken in the Reviewers' laboratory on the involvement of the hydrazone fragment in opening the oxide[64–84], epi-imino[85–95], and episulphide[62,96] rings of 16,17-epoxy(epi-imino, epithio)-20-oxo-steroids. The resulting generalisations have been applied to the controlled modification of steroidal compounds. The stereochemical aspect and the mechanism have been studied in detail on 16,17-epoxy-ketones, with examination of the influence of the stereochemistry of the initial oxide on the stereochemical direction

in which the oxide ring is opened by nucleophilic reagents[63,97].

1. Epimeric 16,17ξ-Epoxy-20-oxo-steroids

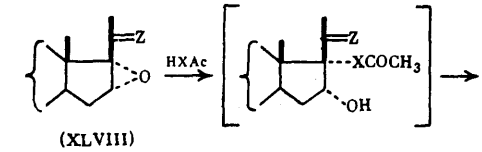
The presence of a reagent for the carbonyl group (a hydrazine) produces a marked change in the direction of ring-opening in 16,17-epoxy-ketones. In all cases regio-specific *cis*-opening of the ring is observed at the position closest to the hydrazone group; the general reactivity of the system towards ring-opening reactions is appreciably enhanced. Hydrazine plays a direct part in the reactions, adding to the keto-group by the stage preceding ring-opening[75,81,83] and forming the 20-hydrazone of the corresponding oxide[64,76-78]. With the above general structural direction of opening in 20-hydrazones of epimeric 16,17α-epoxy-ketones the final result is different and depends solely on the stereochemistry of the oxide ring.

The general scheme of ring-opening in 16,17α-epoxides in the presence of ethyl hydrazine carboxylate is

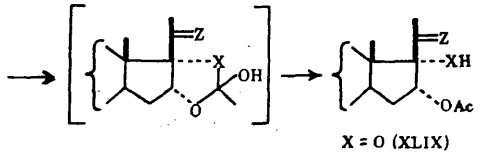


Nu = OH[65], OCH_3[67], OAc[64], SAc[71, 72], N_3[68-70], SCN[73, 74]
$Z = NNHCO_2C_2H_5$

where the reagents used for this purpose are enumerated. All the reactions take place stereo- and regio-specifically with *cis*-opening of the oxide ring at the tertiary carbon atom and incorporation of the reagent from the rear of the molecule. The *cis*-position of the resulting vicinal group quite often favours secondary cyclisation involving these substituents, a particular case of which is acyl migration. Thus reaction of the epoxide (I) with acetic and thioacetic acids under conditions of *cis*-opening[64,71,72] yields the 17α-hydroxy(or mercapto)-16α-acetates (XLIX) or (L), formed by the well-known route[97] via the orthoester intermediate:

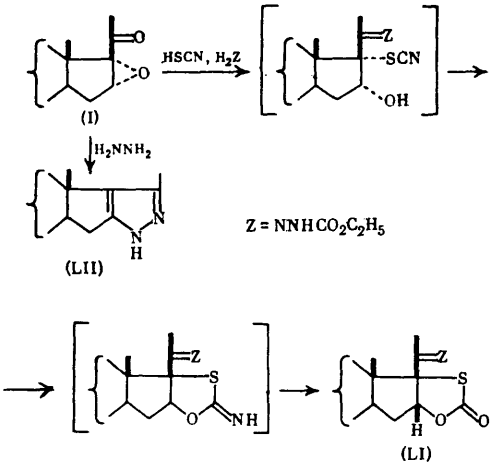


(XLVIII)
$Z = NNHCO_2C_2H_5$, X = O, S



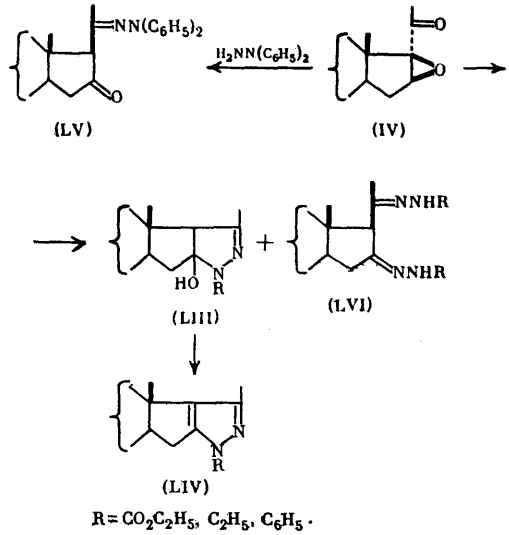
X = O (XLIX)
X = S (L).

The analogous reaction of the hydrazone (XLVIII) with thiocyanic acid yields the thiocarbonate (LI):



Exclusion of the nucleophilic reagent from the reaction medium directs the reaction of 20-hydrazones of 16,17α-epoxides towards cyclisation and formation of the pyrazole (LII).[83] This competes with the main reaction of (XLVIII) with thioacetic acid[72].

Incorporation of nucleophilic reagents is not observed in the ring-opening of 20-hydrazones of epimeric 16,17β-epoxides. Intramolecular cyclisation predominates, yielding the hydroxypyrazoline (LIII), which eliminates water to form the pyrazole (LIV):[78,79]

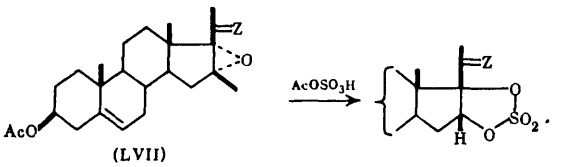


$R = CO_2C_2H_5$, C_2H_5, C_6H_5.

Use of diphenylhydrazine as reagent for a keto-group directs the process towards formation of a monohydrazone of the diketone (LV):[80,84] the second keto-group is not replaced by a hydrazone residue owing to steric hindrance. In several cases, e.g. in the presence of excess of ethyl hydrazinecarboxylate in acetolysis of the 16,17β-epoxide (IV), the dihydrazone (LVI) is formed together with the pyrazoline (LIII).[78] Complete elimination of deuterium in *cis*-ring-opening of the 16-deuterated 16,17β-oxide (IV) by acetic acid in dioxan indicates that these reactions occur with detachment of a proton from the $C_{(16)}$ atom and formation of the Δ^{16}-16-ol, which is then stabilised either by

intramolecular cyclisation involving the hydrazone fragment or by ketonisation[84].

The ditertiary 16β-methyl-16,17α-oxide (VIII) is an extremely interesting but little studied compound undergoing *cis*-ring-opening[46,98,99]. Both substituents adjacent to the epoxide, apparently involved in destabilising the carbocations formed when its ring opens, should promote cleavage of the epoxide bond in both directions. Nevertheless, the heterocycle in the epoxide hydrazone (LVII) is inert towards the ring-opening reactions of hydrolysis and acetolysis catalysed by mineral acids[98]. More severe conditions cannot be applied to the oxide 20-hydrazones owing to initial hydrolysis of the hydrazone group. Perhaps the only ring-opening reaction of the 16β-methyl oxide (LVII) that has been studied is the action of acetylsulphuric acid, which goes formally in the same direction as the corresponding reaction with the 16β-methyl-20-oxo-16,17α-oxide (VII):[46]



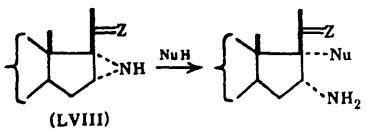
(LVII)

Z = $NNHCO_2C_2H_5$

2. *cis*-Ring-opening of 20-Hydrazones of 16,17α-Epi-imino-steroids

The synthetic aspect of *cis*-opening has been extended significantly to 16,17α-epi-imino-20-oxo-steroids[85-95,100,101]. They exhibit several general features—(*a*) high reactivity, exceeding by several times that observed for the epoxy-analogues, (*b*) addition of hydrazine at the keto-group in the stage preceeding ring-opening, (*c*) exclusive stereo- and regio-specificity of ring-opening at the position adjacent to the hydrazone fragment, and (*d*) occurrence under the reaction conditions of secondary cyclisation processes involving the 16,17α-*cis*-group formed—independently of the presence or absence of an *N*-substituent. A mechanism of *cis*-opening suggested for 16,17-epoxy-steroids has been extended to reactions involving 16,17α-epi-imino-ketones, and used to explain the changes observed[100].

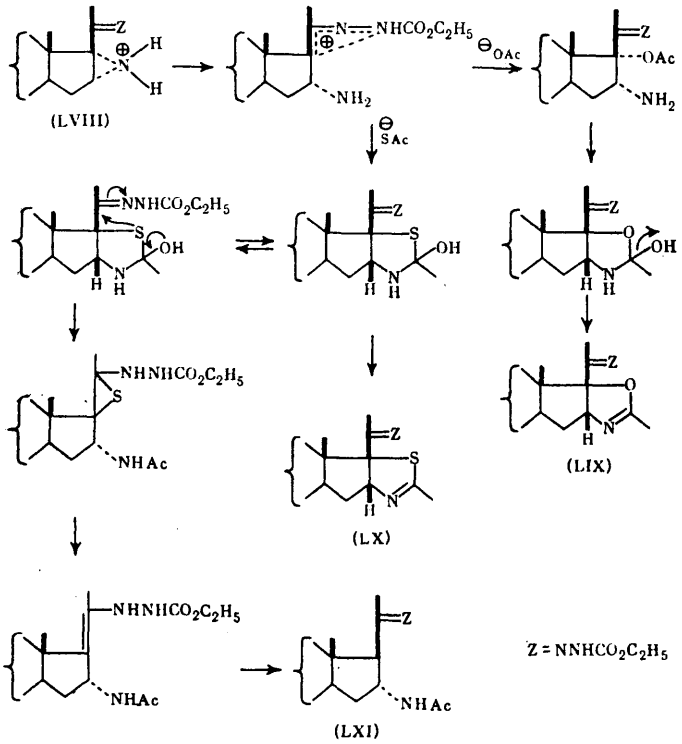
Exclusive incorporation of the nucleophilic reagent in the α-position to the hydrazone fragment from the rear of the molecule has been recorded in reactions of the 20-hydrazone (LVIII) with such reagents as hydrazoic acid[90,91,94], hydrogen fluoride[95], hydrogen chloride[88], water[87], and hydrogen sulphide[93], with formation of the 20-hydrazones of the corresponding products of *cis*-opening of the heterocycle:



(LVIII)

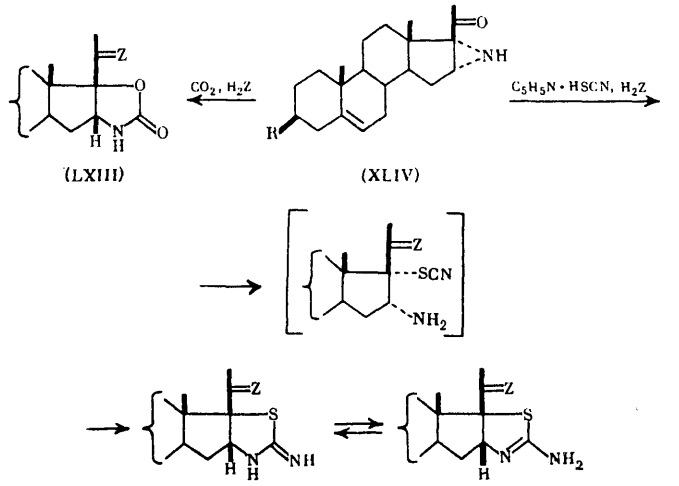
Z = $NNHCO_2C_2H_5$; Nu = N_3, F, OH, SH, Cl.

Attack by acetate (or *S*-thioacetate) ions at the $C_{(17)}$ atom in reactions of the epi-imine (LVIII) with acetic[85] and with thioacetic[86] acids is completed by cyclisation by the ortho-ester mechanism with formation respectively of the 2'-methyl-oxazoline (LIX) at the 2'-methylthiazoline (LX); water is eliminated at the stage of orthoester formation:



It is assumed that, in the action of thioacetic acid on the hydrazone (LVIII), stabilisation of the orthoester intermediate by intramolecular attack by sulphur at the $C_{(20)}$ atom in conformity with the above scheme leads to formation of the amide (LXI) as well as the thiazoline (LX).

Thiocyanic acid acts on the epi-imine (XLIV) to produce *cis*-ring-opening in the general direction, leading to incorporation of the thiocyanate ion in the vicinal position to the hydrazone group followed by cyclisation to a 2'-iminothiazolidine in tautomeric equilibrium with the 2'-aminothiazoline form (LXII):[86]

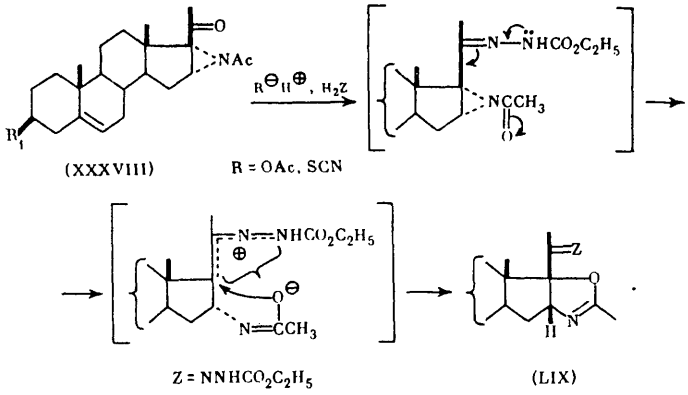


(LXII)

R = OH, OAc; Z = $NNHCO_2C_2H_5$.

The stereochemical requirements of reactions involving expansion of a three-membered to a five-membered ring suggest initial *trans*-opening followed by cyclisation, so that such reactions are atypical in polycyclic systems. It is interesting in this connection that the epi-imino-ketone (XLIV) reacts readily with carbon dioxide in the presence of ethyl hydrazinecarboxylate to form the oxazolidinone (LXIII): i.e. the favourable stereochemistry of ring-opening makes this process entirely feasible[101].

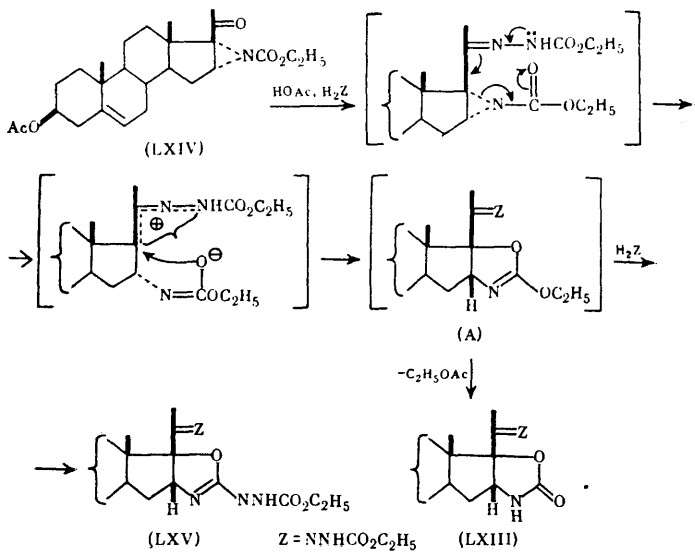
The general direction of ring-opening in *N*-substituted 16,17α-epi-imino-ketones in the presence of ethyl hydrazinecarboxylate does not differ fundamentally from that of their unsubstituted analogues, but stabilisation of the resulting 17-carbocation is effected not by incorporation of an external nucleophile but by intramolecular isomerisation involving an internal nucleophile. As a consequence, independently of whether an external nucleophile is or is not present, reaction with the *N*-acetylepi-imine (XXXVIII) results in formation of the oxazoline (LIX):



(XXXVIII) R = OAc, SCN

Z = $NNHCO_2C_2H_5$ (LIX)

The synthetic possibilities of the reaction can be extended by varying the *N*-substituent to obtain various new types of steroid heterocycles with a nitrogen atom attached to $C_{(16)}$. Thus formation of the oxazolidinone (LXIII) and its 2′-hydrazine derivative (LXV) in the reaction of the 16,17α-ethoxycarbonylepi-imine (LXIV) with ethyl hydrazinecarboxylate in acetic acid involves nucleophilic intramolecular cyclisation affecting the ethoxycarbonyl group[92,101]:



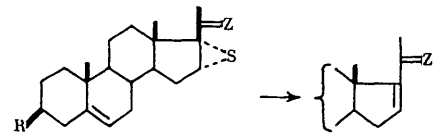
(LXIV) (A)

(LXV) Z = $NNHCO_2C_2H_5$ (LXIII)

It is assumed that the intermediate 2′-ethoxyoxazoline (A) reacts further by two independent paths: it either undergoes attack by the acetate anion with elimination of ethyl acetate or it condenses with a second molecule of ethyl hydrazinecarboxylate.

3. Opening of the Three-membered Ring in Ethoxycarbonylhydrazones of 16,17α-Epithio-steroids

Replacement of the oxo-group by a hydrazone fragment in 16,17α-epithio-20-oxo-steroids, in contrast to the above reactions of the 16,17α-epoxy(and epi-imino)-analogues, does not enhance the general reactivity of the episulphide ring. Moreover, the 20-ethoxycarbonylhydrazone of the 16,17α-epithio-ketone (LXVI) even exhibits some decrease in such reactivity, with an enhanced tendency to eliminate sulphur. It is sufficient to mention that, under the conditions of preparation (acetic acid and ethyl hydrazinecarboxylate at 20 °C), this hydrazone (LXVI) is converted partly—and to a greater extent with increase in exposure—into the alkene (LXVII):



(LXVI) (LXVII)

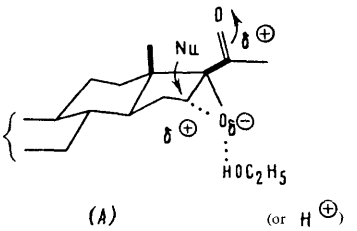
R = OH, OAc; Z = $NNHCO_2C_2H_5$.

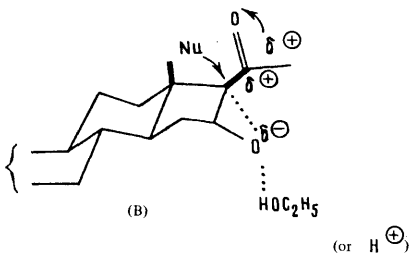
Reactions of the hydrazone (LXVI) have been studied with a wide range of reagents—water, methanol, acetic, thioacetic, and thiocyanic acids, the pyridine complexes of thiocyanic acid and of hydrogen fluoride, hydrazoic acid, ethanethiol, and phenylmethanethiol—but in no case has incorporation of the reagent been detected[96]. The reaction of the hydrazone (LXVI) with ethanethiol is exceptional: nuclear magnetic resonance spectroscopy and elementary analysis show that the chromatographically difficultly separable mixture of reaction products contains, together with the alkene (LXVII) and products formed by subsequent addition of the thiol to it, also a compound resulting from addition of the mercaptide ion to the episulphide ring.

VI. FACTORS CONTROLLING OPENING OF A THREE-MEMBERED RING

The above facts show that in these keto-oxides the classic *trans*-scission of the oxide ring at the β-position to the carbonyl group is most often (not always) evident only among 16,17α-epoxy-20-oxo-steroids. It appears useful to discuss the results systematised above in terms of a "borderline" or "modified" S_N2 substitution mechanism[3], which has become the most acceptable theoretical model for describing the opening of epoxide rings. According to this mechanism reaction between the oxide and a nucleophilic reagent involves a termolecular transition state, in which almost synchronous action of the nucleophilic reagent and an electrophilic "accomplice" (solvent or catalyst) causes rupture of a carbon–oxygen bond. The transition state of a "modified" reaction having an S_N2 mechanism has longer partial bond lengths than has the classic S_N2 mechanism, with rupture of the carbon–oxygen bond in the oxide always more pronounced than formation of the new carbon–nucleophile bond. This is evident in the appearance in the transition state of a partial positive charge on the carbon

atom of the reaction centre, the possibility of whose stabilisation determines the principal direction of ring-opening. Hence *trans*-opening of 16,17α-epoxy-20-oxo-steroids must be described in terms of the transition states





resulting from attack by the nucleophilic reagent from the front of the steroid molecule on the secondary and the tertiary centre respectively.

It can be assumed that transition state (A) is preferred not only because mutual repulsion between the two adjacent centres in (B) increases its activation energy[2] but also because the cationoid character of the $C_{(17)}$ centre in the latter is in some measure suppressed by the oxide ring in the preferred *S-trans*-conformation (Fig. 1*a*),[16,17,102] whose geometry satisfies the optimum requirements for conjugation of the keto-group with the oxide ring[7,12]. Furthermore, polar shielding by the neighbouring keto-function in the preferred conformation (*a*), and also the need for equatorial attack by the reagent in *trans*-opening of the oxide, do not favour realisation of transition state (B). The observed high stereo- and regio-selectivity of ring-opening reactions of 16,17α-epoxy-20-oxo-steroids with strong nucleophiles must then be explained by their occurrence via transition state (A), preference for which is due to concerted action of the conformational factor (*trans*-quasi-axial opening and attack from the opposite side of the oxide ring) and the electronic factor (electron-accepting influence of the keto-group when conjugated with the epoxide ring in the preferred *S-trans*-conformation).

Comparative analysis of steric factors in the intermediate species (A) and (B) does not support preference for either. Indeed, approach of the nucleophile to the $C_{(17)}$ and $C_{(16)}$ atoms is sterically hindered approximately equally by the angular and the $C_{(21)}$ methyl group in the *S-trans*-conformation, except that this involves respectively 1,3- and 1,2-interaction. This is why reactions with weak nucleophilic reagents take place in both directions, their result apparently depending on the relative rates of neutralisation of the two intermediate species. In particular, neutralisation of the carbocation centre at the $C_{(17)}$ atom by migration of the angular methyl group is more rapid than the alternative addition of a weak nucleophile (e.g. water) to the $C_{(16)}$ centre. In the absence of a nucleophilic reagent this becomes the sole reaction.

The geometry of ditertiary 16,17α-epoxy-16β-methyl-ketones differs from that of the desmethyl analogues. The preferred conformation of 16β-methyl-16,17α-epoxides is (*b*) (Fig. 1), in which the keto-group is oriented above the D ring in a skew position relative to the $C_{(13)}$–$C_{(17)}$ bond[17,102]. The general balance of steric and electronic factors changes in such a molecule (conjugation breaks down and the β-region of the molecule is strongly shielded), which by no means favours nucleophilic attack on the $C_{(16)}$ atom by an S_N2 mechanism. Therefore acid opening of the oxide ring in compounds of this type involves exclusively rupture of the $C_{(16)}$–O bond by a unimolecular mechanism with formation of a 16-carbocation, whose stabilisation is favoured by the 16-methyl group. Neutralisation is effected either by elimination of a neighbouring proton or by *cis*-opening of the oxide ring from the rear of the molecule[44].

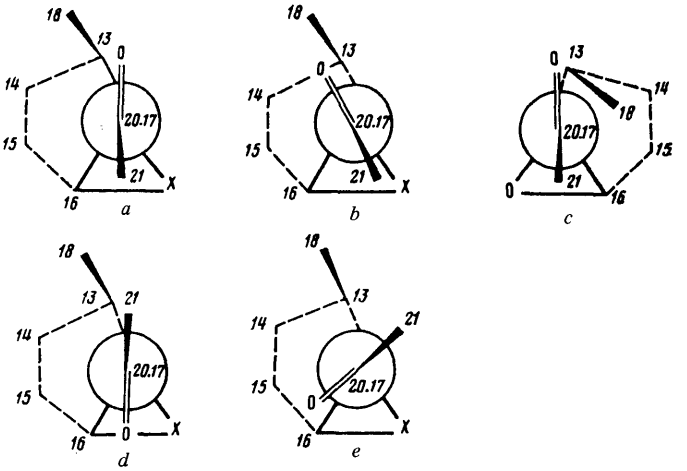
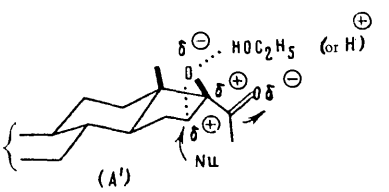
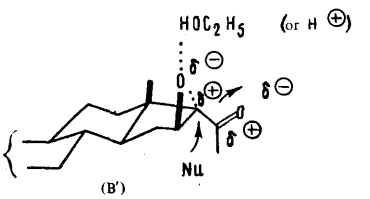


Figure 1. Newman projections of the conformations of 16,17-hetero-substituted 20-oxo-steroids, produced by rotation about the $C_{(17)}$–$C_{(20)}$ bond. The numerals denote carbon atoms.

In 16,17β-epoxy-20-oxo-steroids the general balance of factors controlling the structural direction and the stereochemistry of opening of the oxide is changed. Examination on the same basis of molecular models and of the intermediate states





shows that the total of factors promoting attack at the $C_{(16)}$ atom remains unchanged, whereas the number of factors opposing attack at the $C_{(17)}$ atom diminishes. The most important and apparently decisive difference between transition states (A') and (B') is that the conformational factor—*trans*-quasi-axial attack at the $C_{(17)}$ atom—promotes opening of the 16,17β-oxide at the tertiary $C_{(17)}$ atom. Furthermore, approach of the nucleophilic reagent to $C_{(17)}$ from the rear of the molecule is sterically less hindered in (B')§. The thermodynamic factor is favourable also to formation of products with a β-configuration of the 17-acetyl group on ring-opening of 16,17β-epoxy-20-ketones. All these considerations make *trans*-attack by the nucleophilic reagent at the tertiary centre in the opening of 16,17β-epoxy-ketones logically understandable, but it is difficult in the general logic of the argument to explain their *cis*-opening at this centre, and also the Wagner–Meerwein rearrangement. It can therefore be supposed that the transition state of carbocation type (B') formed in the modified S_N2 mechanism is characterised more by breakage of the old bond than by formation of a new bond, with consequent smaller steric hindrance to attack from the β-region.

Most of the ring-opening reactions of keto-aziridines, both basic (including protonated) and activated, are classified as substitutions, in which S_N2 and S_N1 mechanisms compete depending on the structure of the aziridine and the reagent[6]. The observed *trans*-stereochemistry of the opening of 16,17α-epi-imino-ketones and their *N*-acetates indicates reactions of type S_N2. This applies equally to those involving rupture of the $C_{(17)}$–N bond, for an S_N1 substitution would be expected to yield not only products of a Wagner–Meerwein rearrangement but also those of attack at the $C_{(17)}$ carbocation from the rear, less hindered side of the molecule. Differences in reactivity between 16,17α-epi-imino-ketones and their structurally similar epoxy-analogues must apparently be explained, in terms of an S_N2 substitution mechanism, by the difference in their geometry shown in the Newman projections in Fig.1.[15,17,102] The *S*-cisoid conformation (*d*) is assumed for the aziridine (XLIV), with the keto-group and the *N*-proton involved in an intramolecular hydrogen bond. In the preferred conformation of the *N*-acetylaziridine (XXXVIII) the keto-group is displaced from conjugation with the ring and skew to the $C_{(16)}$ centre inside ring D, with both acetyl groups *cis*-oriented with respect to the plane of the aziridine ring (Fig.1*e*). The lower reactivity of the aziridine (XLIV) in ring-opening involving the $C_{(16)}$ centre than of epoxides, and its tendency to isolated addition both at the keto-group and at the aziridine ring, are explained by the difference in conformation between the initial molecules and the consequent change in balance of steric and polar factors[102]. This provides an explanation also of the low reactivity of the *N*-acetates (XXXVIII), in which strong polar shielding by the two carbonyl functions of the acetyl groups prevents approach of a nucleophilic reagent to the $C_{(16)}$ atom.

Epithio-ketones are far less reactive than their oxygen analogues, but still show a tendency to the same direction of ring-opening. The episulphide (XLVI) is a conformationally more labile model than the epoxy-analogues, but the conformational mobility of the 17β-acetyl group is restricted to conformations having *trans*-orientation of the keto-group and the heterocycle, with the *S-trans*-conformation (Fig.1*a*) showing minimum energy, and 30° deflection of the 21-methyl group towards coplanarity of the keto-group and the $C_{(17)}$–S bond energetically preferred to displacement in the opposite direction[103,104]. The factor stabilising the system in the preferred *trans*-conformation is apparently orbital interaction of the carbonyl with the delocalised electronic system of the episulphide ring. The difference in character between this interaction in the episulphide (XLVI) and in the epoxide (I) is evident from Fig.2, which illustrates the distribution of electron density obtained by quantum-chemical calculation in the energetically preferred conformations of the ground state of a fragment of the D-ring in (I) and (XLVI) with an indication of the bond lengths determined by X-ray structural analysis[16,103,104]. The episulphide shows diminished electrophilicity of the carbon centres at the points of attack and also diminished polarisation of its keto-group, the latter obviously due to displacement of the electron shell from the carbonyl group to a vacant *d*-orbital of the sulphur atom[105–107]. It may be supposed that these electronic differences together with the establishment of a conformation sterically favourable for elimination of sulphur, with anti-coplanar arrangement of keto-group and $C_{(17)}$–S bond, are responsible for the above behaviour of the episulphide in ring-opening reactions.

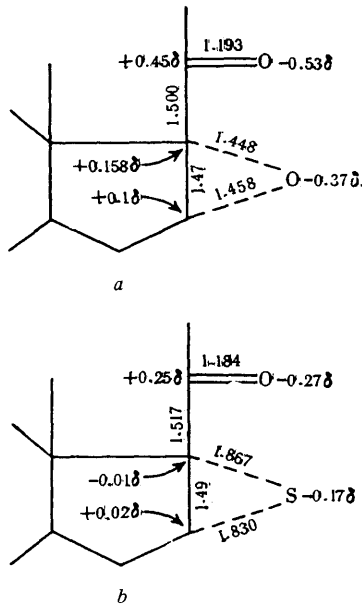
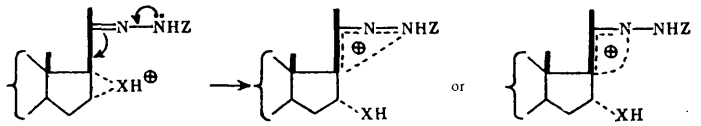


Figure 2. Distribution of electron density on atoms of the D-ring obtained by quantum-chemical calculation and interatomic distances (Å) determined by X-ray structural analysis for the: *a*) epoxide (I); *b*) episulphide (XLVI).

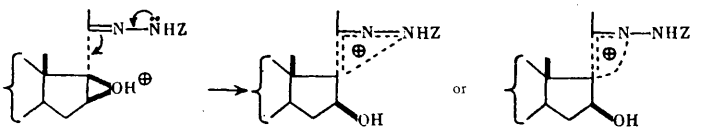
§By analogy with 16,17α-epoxides the preferred conformation of 16,17β-epoxy-20-oxo-steroids is taken to be (*c*) (Fig.1), with *anti*-orientation of the oxygen functions (oxo- and epoxy-groups).

Replacement of the keto-group by a hydrazone fragment apparently reverses completely the direction of polarisation of the system[63]. Under acid conditions reversible electronic displacement of the lone pair of the amino-nitrogen atom along the conjugated chain becomes more characteristic,

with a consequent loosening of the heterocyclic $C_{(17)}$–X bond (X = O, NH, $NCOCH_3$). At present, unfortunately, experimental information on the mutual steric arrangement of hydrazone group and three-membered ring is lacking. However, the fact that the configuration at $C_{(17)}$ is strictly maintained indicates rather preference for the *S*-transoid conformation. On the basis of the experimental facts it is suggested as intermediate species a non-classical cyclic ion stabilised in the configuration of the initial oxide or aziridine hydrazone:



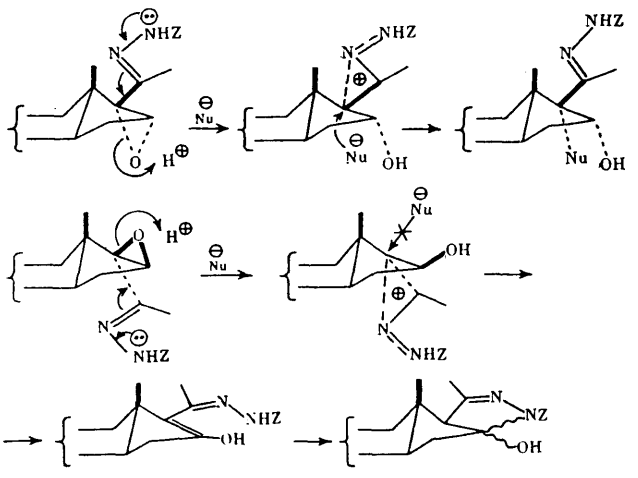
X = O (XLVIII)
X = NH (LVIII)
X = NAc



Z = $CO_2C_2H_5$.

The question of whether both hydrazone nitrogen atoms are involved in this interaction or only that closer to the ring remains open[63].

Two factors—presence of a nucleophilic reagent and possibility of its approach to one side or the other of the non-classic cation—govern the subsequent fate of the latter. In the 20-hydrazone of the 16,17α-oxide the configuration of the cation requires approach of the reagent from the rear of the molecule. As a consequence, in the presence of a nucleophile the reaction is completed by its incorporation at $C_{(17)}$, and in the absence of such a reagent by elimination of a proton from the $C_{(16)}$ atom followed by intramolecular cyclisation involving the hydrazone fragment:



Z = $CO_2C_2H_5$, C_6H_5.

The reason for the observed course of the reaction in the latter case is the impossibility of any other way of satisfying the electronic requirements of neutralisation of the non-classical cation. The configuration of the cation of the 16,17β-epoxide 20-hydrazone requires that a nucleophile should attack from the side of the sterically-shielded β-region of the molecule. As a consequence, its neutralisation is effected not by addition of the nucleophile from the side of the β-epoxy-group but by elimination of a neighbouring proton with formation of a Δ^{16}-enol, which either rearranges into a ketone or cyclises into a pyrazolinol. But the latter role in the general direction of ring-opening reactions of oxide 20-hydrazones is apparently played by the geometrical arrangement of the hydrazone fragment relative to the plane of the three-membered ring, although this aspect has remained almost uninvestigated.

The anomalous behaviour of the 20-hydrazone of the 16,17α-epithio-ketone (LXVI) in ring-opening reactions suggests a different mechanism of interaction of the episulphide ring and the hydrazone fragment, without formation of an intermediate non-classical carbocation.

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Advances in the Chemistry of α-Halogenoallenes

M.V.Mavrov

Results obtained on the preparation and reactions of α-halogenoallenes are critically surveyed, and the reaction mechanisms are discussed. A list of 224 references is included.

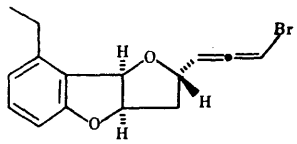
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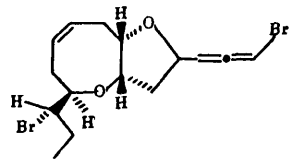
I. INTRODUCTION

α-Halogenoallenes are important examples of organic compounds having cumulative double bonds. As polyfunctional compounds they have an interesting structure, on whose basis various compounds can be obtained having properties useful in many fields of organic synthesis and practical application.

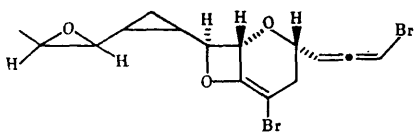
Individual members of this class, containing a terminal bromoallene group, have already been found in Nature. Thus the phenyl ether panacene



panacene



laurallene



okamurallene

has been isolated from the mollusc *Arlysia brasiliana*[1], and the bicyclic diethers laurallene and okamurallene have been obtained[2] from the marine red algae *Laurencia*.

During recent years research in this field has become more active and systematic, but the results have not yet been covered in reviews[3-6].

II. METHODS OF PREPARATION

Halogenoallenes can be obtained in various ways. In several cases these methods are based on elimination. However, most typically halogen substituents are introduced, and form the basis for various rearrangements of acetylenic compounds.

1. 1,2-Elimination

Practical methods for obtaining halogenoallenes by elimination are at present restricted to the dehalogenation and dehydrohalogenation of aliphatic compounds containing mainly halogens as substituents[4].

Mono- and di-fluoropropadienes have been prepared by the action of zinc in alcohol[7] or in dimethylformamide[8]. Debromination of 2,3-dibromo-1,1,3,3-tetrafluoropropene (with magnesium in oxolan) gives a 91% yield of perfluoroallene[9]. Butyl-lithium metallates 2-bromo-3,3,3-trifluoropropene at the bromine, which undergoes elimination when the temperature is allowed to rise from −90 to 20 °C, to give a 72% yield of 1,1-difluoroallene[10]:

$$CF_3C(Br)=CH_2 \xrightarrow{BuLi,\ -90^\circ} CF_3C(Li)=CH_2 \rightarrow CF_2=C=CH_2 .$$

Deiodofluorination in the presence of copper powder at 200 °C has been used to obtain theoretical yields of perfluoro-1,2-dienes[11]:

$$CF_3CCl=C(R)CF_3 \rightarrow CF_2=C=C(R)CF_3 \qquad R=C_2F_5,\ n\text{-}C_3F_7,\ iso\text{-}C_3F_7 .$$

Various basic reagents–alkalis in a solvent[12-15] or in the solid state[16], sodamide in liquid ammonia[17,18], butyl-lithium[19]– are used to effect β′-elimination. This method can be employed to obtain trifluorinated[16], perfluorinated[12-14], perchlorinated[17], and perbrominated[18] allenes.

Dibromoalkenes containing substituents Y = COOR, COR, $PO(OC_2H_5)_2$, which activate an α-hydrogen atom, are readily dehydrobrominated by bases, including amines, to give satisfactory yields of allenes BrCH : C : CHY.[20-24] Potassium or lithium t-butoxide is used at low temperatures to prepare perhalogenoallenes containing electron-accepting groups[25,26]:

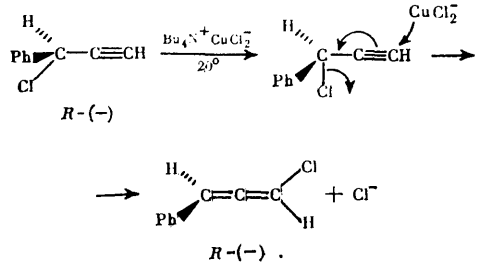
$$CCl_2=C(X)-CH(Cl)Y \xrightarrow{-70^\circ} CCl_2=C=C(Cl)Y \qquad Y=CO_2Et,\ CN,\ CONH_2 .$$

2. Prop-2-ynyl Rearrangements

Anionotropic conversion

Many reagents are able to convert 3-halogenoalkynes into 1-halogenoallenes, among which the most commonly used are copper(I) salts[27-29]. Although this process is reversible, it is often possible under appropriate experimental conditions to obtain entirely satisfactory yields (40–70%) of α-halogenoallenes[29-32]. Under the influence of the tetrabutylammonium chloride complex of copper(I) chloride(−)-phenylprop-2-ynyl chloride is converted with high stereospecificity into the optically active allene chloride[33]. In view of the first order a single-stage mechanism of S_N2' type with *anti*-attack by

the reagent is assumed for this reaction:



R-(−) .

Prototropic isomerisation

Only a few examples of the prototropic isomerisation of halogeno-compounds have been reported. Thus in the presence of sodium ethoxide a diacetylenic bromide isomerises into an allene[34]:

$$(RC{\equiv}C)_2CHBr \xrightarrow{EtONa} \underset{\displaystyle Br}{RC{\equiv}CC{=}C{=}CHR} \qquad R = t\text{-}Bu\ .$$

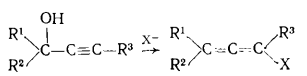
Isomerisation can be arrested at the stage of allene formation when electron-accepting groups activate the initial molecule. For example, halogenoallenecarboxylic esters are formed under very mild condtions[35,36], on brief shaking with dilute potassium carbonate solution at room temperature. Isomerisation is not observed in the absence of stabilising groups, as is clearly shown by the bromoprop-2-ynyl ester[35]:

$$BrC{\equiv}CCH_2\overset{\displaystyle O}{\overset{\|}{C}}OCH_2C{\equiv}CBr \xrightarrow{OH^-} BrCH{=}C{=}CH\overset{\displaystyle O}{\overset{\|}{C}}OCH_2C{\equiv}CBr\ .$$

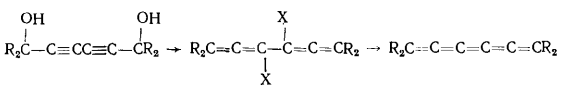
Prototropic isomerisation is possible under radical conditions[31,37]. A photochemically generated bromine atom leads to partial isomerisation of bromoprop-2-ynyl into bromoallenyl[37].

Anioniotropic rearrangements

It is well known that acetylenic compounds containing a group X = H, Hal, OH, MgZ, etc. in the prop-2-ynyl position are able to give an allene product on undergoing an S_N2' substitution[4,5]. Various α-halogenated allenes can be obtained from acetylenic alcohols as a result of this reaction:



Primary, secondary, and tertiary alcohols having a terminal triple bond and containing various types of alkyl groups near the reaction centre readily undergo the reaction[18,28,38–48]. It has acquired greatest value for the preparation of persubstituted halogenoallenes with aliphatic[43,47,49–51], aromatic[52–55], and alicyclic[56–58] substituents when the yields are 70–90%. Functional halogenoallenes—polyhalogenated[47,59–62], containing ester [63,64] and heteroatomic groups[65–68]—have also been obtained by this method, but side-reactions lower the yields. When two active centres are present, good yields can be obtained of dihalides having conjugated allene groups[51,56,59], which have found application in the synthesis of cumulenes[69,70]:

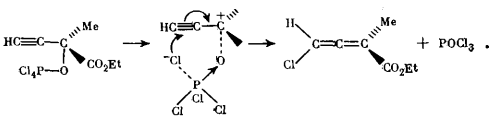


R = t-Bu, Ph, 2,2,6,6-$(CH_3)_4$-cyclo-C_6H_7;
X=Cl, Br .

The hydroxy-group is exchanged for a halogen atom when alcohols are treated with hydrohalic acids—hydrochloric[28,44,47,50], hydrobromic[39,40,43,47,59,60,67], and hydriodic[47,60]—phosphorus trichloride[49] and pentachloride[61,64] thionyl chloride[42,44–49,51–55,57,60,61,63], phosphorus tribromide[41,42,46,49,52,53,56,71], sulphuryl bromide[64], phosphorus pentabromide[64,71], and a mixture of triphenyl phosphite and iodomethane[38,68]. The detailed course of the reactions has not been studied, but qualitative observations show the possibility of varying and experimental conditions within each class to enable satisfactory results to be obtained. The yields differ somewhat, but under the most favourable conditions reach 70–90%.

Additional information on the chemistry of the reactions has been gained by the use of optically active substrates. Study of the action of three of the above reagents—thionyl chloride[45,72,73], hydrobromic acid[43], and phosphorus pentachloride[74]—on optically active acetylenic alcohols has shown high stereoselectivity of formation of halogenoallenes, usually with retention of configuration.

Intermediate products in all these reactions are probably chlorosulphite[63,73], a copper complex coordinated with hydroxyl and ethynyl groups[43], or a prop-2-ynyl cation solvated by phosphoryl chloride[74], which break down as a result of internal electron transfer: e.g.



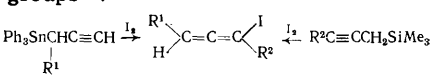
Thus the halogen is introduced as a consequence of *cis*-nucleophilic substitution by an S_Ni' mechanism.

Other reactions are known involving exchange of a prop-2-ynyl function for halogen. Thus the action of iodine on a 4-chlorobut-2-ynoic ester forms the 2-iodobutadienoic ester[75].

Iodoallenes have been obtained by reaction between prop-2-ynyl bromide and iodine in methanolic caustic potash[76,77]; all three hydrogen atoms may be substituted:

$$HC{\equiv}CCH_2Br \xrightarrow{I_2} IC{\equiv}CCH_2I \xrightarrow{I_2} I_2C{=}C{=}CHI \xrightarrow{I_2} I_2C{=}C{=}CI_2\ .$$

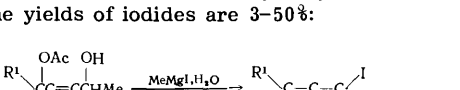
The suggested mechanism involved an intermediate allene carbanion. Similarly, phenylprop-2-ynyl chloride and *para*-substituted phenylprop-2-ynyl sulphide give 40–65% yields of the corresponding tri-iodoallenes[77]. Iodides are formed also by direct replacement of the triphenylstannyl[78] and trimethylsilyl groups[79]:



R^1=H, Me; R^2=C_6H_{13} .

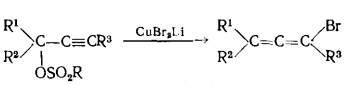
This method is suitable also for obtaining allenyl bromides[79].

Monoacetates of acetylenic t-glycols react with methylmagnesium iodide, but a mixture of products is formed, including allene iodides[80]; after hydrolysis of the reaction mixture the yields of iodides are 3–50%:



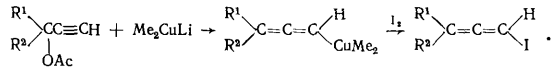
R^1, R^2=Alk, Ph .

Allene bromides are formed in ~60% yields also from prop-2-ynyl sulphonates by the action of the lithium copper(I) bromide complex in[81]:

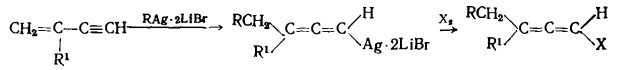


R=Me, *p*-Me-C_6H_4; R^1, R^2, R^3=H, Alk, Ph .

New methods of synthesis are based on reactions of allene organometallic compounds. Thus an organocopper intermediate, prepared regiospecifically from prop-2-ynyl acetates with lithium dimethylcuprate, reacts normally with iodine (at −78 °C) to give allene iodides[82]:



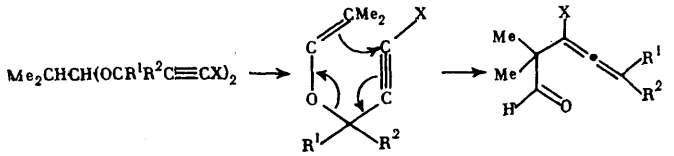
In the same way an allenylsilver salt (obtained by 1,4-addition of an alkylsilver(I)–lithium bromide complex to homologues of butenyne) is able to react with electrophiles (including halogens) to form brominated (iodinated) allenes[83], accompanied by a small quantity of an acetylenic isomer:



R = n-Bu, t-Bu, iso-Pr; R^1=H, Me; X=Br, I .

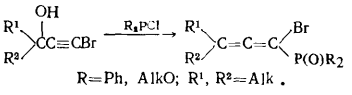
Other rearrangements

Bishalogenoprop-2-ynylacetals, when heated (to 80–115 °C) in the presence of toluene-*p*-sulphonic acid, rearrange *in situ* into halogenoallene aldehydes[84,85]. It is assumed that a Claisen-type rearrangement takes place with intermediate formation of a prop-2-ynyl vinyl ether:



R^1, R^2 = H, Alk; X = Cl, Br .

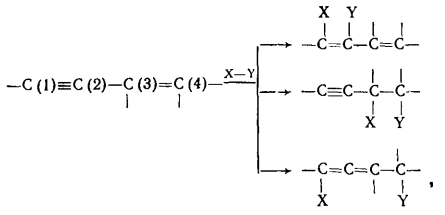
An analogous rearrangement occurs in the reaction between a halogenoprop-2-ynyl alcohol and a dialkyl chlorophosphite[86] or diphenylchlorophosphine[87,88] in the presence of a base, when a halogenoallene derivative is formed in 10–60% yield:



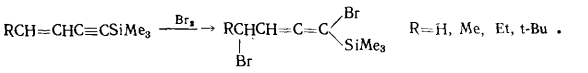
R=Ph, AlkO; R^1, R^2=Alk .

3. Addition to a Conjugated Butenyne System

Addition of molecules X–Y of halogens, hydrogen halides, and other active halogen compounds to conjugated enynes may take place in three main ways[4,89] among which only 1,4-addition yields allenes:

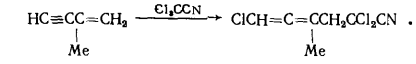


Addition of the different parts of the X–Y molecule obeys the general rule, so that, in conformity with the expected polarisation, the negative group goes to the $C_{(4)}$ atom of the ethylenic double bond. With bromine formation of compounds by 1,4-addition predominates over other directions to such an extent that such addition has preparative value[90–92]:

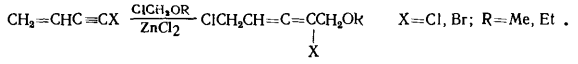


The direction of addition is little affected by the nature of the solvent, although there is a tendency for 1,4-addition to increase with alkenylacetylenes and to a greater extent with trimethylsilyl derivatives[93].

Methylbutenyne reacts with trichloroacetonitrile to give an allene derivative in theoretical yield[94]:

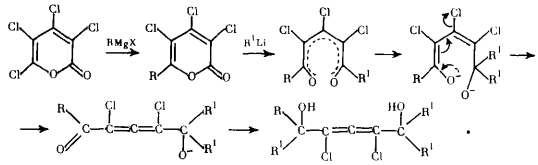


Several examples have been reported of the electrophilic addition of alkyl chloromethyl ethers[95,96] and hydrogen halides[97] to give 30–65% yields of halogenoallenes (although in these cases isomeric dihalides are formed at the same time):

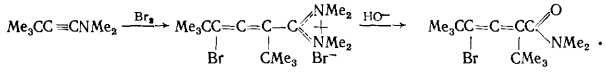


4. Other Methods

Perchloro-2-pyrone reacts with Grignard and then organolithium reagents to give tetra-alkyl-2,4-dichloropenta-2,3-diene-1,5-diols[98], most probably by the scheme



In the bromination of a 3,3-dimethylbut-1-ynylamine addition of a second alkynylamine molecule is observed with formation of the corresponding salt, which under alkaline conditions yields the dimethylamide of 4-bromo-2-t-butyl-5,5-dimethylhexadienoic acid[99]:



III. REACTIONS AND TRANSFORMATIONS

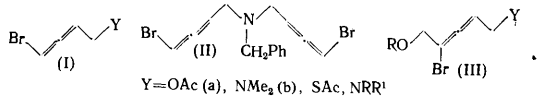
The known chemical reactions of halogenoallenes can be divided into three groups—those leading to functional transformation of substituents without affecting the allene group, cycloaddition, and linear substitution and addition with or without lengthening of the carbon chain.

1. Functional Transformations

Halogenoallenes are extremely sensitive to various reagents and to temperature, which cause a change in the allene bond. They can easily be converted into 1,3-dienes by prototropy[65,84]. It must therefore be borne in mind that the problem of

instability is present in all preparations of functional halogenoallenes.

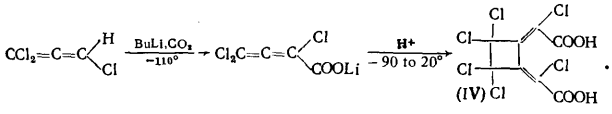
Substitution of the allyl bromine in 1,4-dibromobuta-1,2-diene (I: Y = Br)



Y=OAc (a), NMe_2 (b), SAc, NRR^1

by primary and secondary amines, potassium acetate and thioacetate, and thiourea under mild conditions gives positive results[67,100]. With benzylamine the reaction yields the bisbromoallene amine (II).[101] Functional derivatives of 5-alkoxy-4-bromopenta-2,3-dienes (IIIa,b) have been obtained similarly[96]. 1,4-Dibromobuta-1,2-diene is not hydrolysed under normal conditions: even mild bases (sodium hydrogen carbonate, calcium oxide, silver(I) oxide, etc.) eliminate hydrogen bromide. The alcohol (I: Y = OH) can readily be obtained in 60–70% yield from the acetate (Ia).[102] Trimethylsilyl and oxanyl protection is also readily introduced and removed[67].

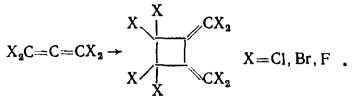
In some cases halogenoallenes undergo deprotonation under the influence of organolithium compounds and form a resonance-stabilised allenylcarbenium ion. But the trichloroallenyl cation reacts in the usual way with carbon dioxide to give the lithium salt of the acid, thermal conversion of which yields (after hydrolysis) and cyclic dimeric product (IV):[19]



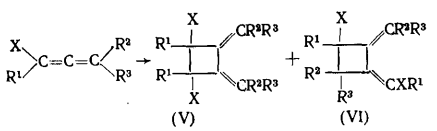
This salt reacts with cyclopentadiene (at −90 to 20 °C) to give in high yield (91%) the adduct of diene synthesis.

2. Cycloaddition Reactions

Dimerisation into four-membered cyclic compounds is a general reaction for the allene group, and is undergone also by halogenoallene derivatives. Indeed, polyhalogenoallenes such as the tetrachlorinated[17,103], tetrabrominated[18,104], and tetrafluorinated[12] propadienes are converted extraordinarily readily even at room temperature (which makes it difficult to obtain them in pure form) into 1,2-bisdihalogenomethylenecyclobutanes:



Thermal 2,2-cycloaddition takes place quite readily with unsymmetrical halogenoallenes, and in several cases (Table 1) yields a mixture of the possible isomers (V) and (VI):



(V) (VI)

The orientation of dimerisation undoubtedly depends on the positions of substituents. Experiment shows that halogenoallenes form four-membered rings head to head (V) and head to tail (VI) at the expense of the halogenated double bond preferably with vicinal methylene groups. Examples of the formation of 1,3-dimethylenecyclobutanes are fairly rare[110]. Nor has addition at both double bonds been reported.

Table 1. Examples of the 2,2-cycloaddition of halogenoallenes.

X	R^1	R^2	R^3	t, °C	Total yield, %	Proportions of isomers (V)	Proportions of isomers (VI)	Ref.
H	H	H	Cl	60	—	100	—	[105]
H	H	F	F	—	—	—	100	[106]
Cl	Cl	Cl	H	20	100	+	+	[107]
Br	H	Br	Br	20	60	100	—	[25]
Cl	Br	Cl	Cl	20	100	100	—	[108]
Cl	H	Me	Me	140	—	45	55	[109]
Br	H	Me	Me	80	28	100	—	[31]
F	C_2F_5	F	F	20	85	26	74	[15]
F	F	CF_3	CF_3	—	—	—	—	[110]
H	H	Cl	CO_2Et	20	—	100	—	[36]
Cl	Cl	Cl	CO_2Et	—	100	100	—	[25]
Cl	Cl	Cl	$CONH_2$	20	—	100	—	[26]
Cl	Cl	Cl	CN	20	—	100	—	[26]
Cl	H	H	mesityl	80	45	41	59	[111]
Cl	H	H	adamantyl	130	90	41	59	[112]
Cl	H	Ph	Ph	—	—	45	55	[109]
Br	H	Ph	Ph	—	—	45	55	[109]
Cl	Cl	Ar	Ar	—	—	100	—	[15]
Cl	H	fluorenylidene		—	—	100	—	[57]
Br	H	fluorenylidene		80	80	—	100	[57]
Cl	t-Bu	T-BuC:C	t-BuC:C	25	—	—	100	[49]
Cl	Cl	Cl	CCl_2COOH	—	—	—	—	[113]
F	F	CF_3	$Re(CO)_5$	—	—	100	—	[114]

Mutual thermal isomerisation of the dimers has been noted in several cases[49,57,110], but the dimer of perfluoroallene in the presence of caesium fluoride isomerises quantitatively into perfluoro-2-methyl-3-methylenecyclobutene[115].

The stereochemistry of dimerisation also depends on the positions of substituents and the degree of substitution of the allene bond. Isomers having a *trans*-arrangement of ring substituents usually predominate in a mixture of stereoisomers[109,112]. Substituents in the two *exo*-methylene groups are arranged mainly in *cis*-positions[111,112]. According to Jacobs[105,111,112] the stereochemical nature of the products of dimerisation is consistent with a biradical mechanism.

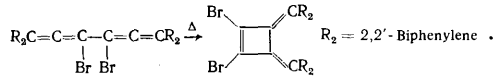
Study of the kinetics and the mechanism of the cyclodimerisation of perhalogenoallenes has shown[103] a second-order reaction. The rate of dimerisation to 1,2-dimethylenecyclobutane derivatives is very strongly dependent on the influence of substituents. Accumulation of electron-acceptors greatly destabilises the system: thus perchloroallene is stable only below −50 °C.[17] Kinetic measurements on a series of halogenoallenes of type $Cl_2C:C:CClX$ show that the rate of dimerisation increases in the sequence of substituents

$$X = H < Br < C_6H_5 \cong Cl < COOC_2H_5 < CN.$$

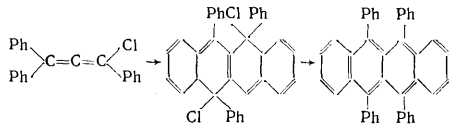
Among these trichlorobuta-2,3-dienenitrile is the most unstable of all allenes known at the present time[26].

Study of the thermodynamics of cyclodimerisation has revealed a low enthalpy of activation (35.2–62.8 kJ $mole^{-1}$) and high negative entropies of activation (−188 to −146 J $mole^{-1}$ deg^{-1}). No paramagnetic intermediate species were detected in the dimerisation of tetrachloroallene, and a non-synchronous two-stage mechanism was assumed[103].

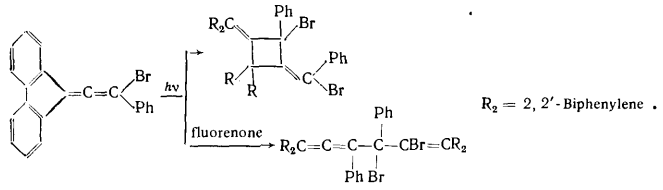
The conjugated 1,6-dibiphenylene-3,4-dibromohexa-1,2,4,5-tetraene when heated undergoes intramolecular cycloaddition with formation of a 3,4-dimethylenecyclobutene derivative[57]:



However, dimerisation of triphenylchloropropadiene takes place preferentially by a Diels–Alder type of reaction accompanied by elimination of hydrogen chloride to form rubrene[116]:

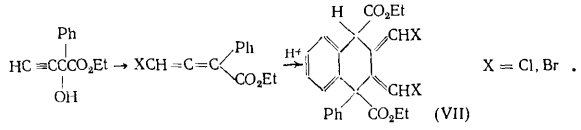


Depending on the conditions photochemical treatment yields various products, including those of 2,2-cycloaddition[111,117]. Thus exposure of 1,1-biphenylene-3-bromo-3-phenylallene in benzene to ultraviolet radiation yields a 1,3-divinylcyclobutane derivative[117]:



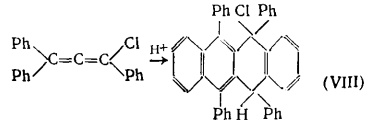
The action of ultraviolet radiation in the presence of fluorenone as sensitiser forms only a product of linear dimerisation of the bromoallene[117].

In several cases the reactions are complicated by interesting rearrangements of the resulting halogenoallenes under the influence of electrophiles. With a 2-hydroxy-2-phenylbut-3-ynoic ester the main product is the cyclic dimer (VII) as a mixture of geometrical isomers relative to the double bond[63,118]:



Formation of such a product can be explained by addition of the cation $XCH:C^{+}C(C_6H_5):C(OH)OC_2H_5$, formed by protonation of the ester group of the halogenoallene, to the central atom of another molecule of the latter followed by an electrophilic substitution type of cyclisation to an aromatic ring[118].

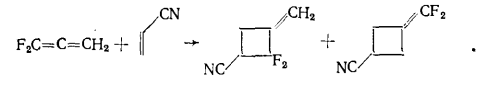
Under the influence of acids triphenylchloroallene undergoes cycloaddition to a tetracyclic compound (VIII):



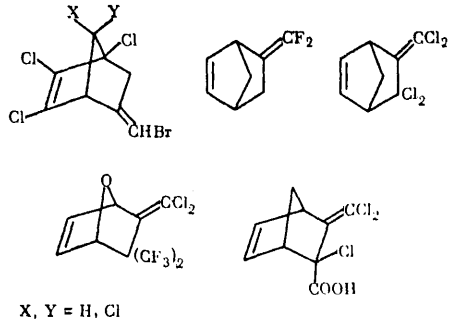
The reaction is assumed to involve interaction of a delocalised carbenium ion formed by protonation of the central carbon atom[119].

The possibility of the codimerisation of halogenoallenes with other dienophiles (X = Y) is strongly dependent on the position and the character of the substituent. The thermal codimerisation of perfluoroallene with hexafluorobutyne at 80–85 °C in the presence of a free-radical scavenger gives a 50% yield of perfluoro-1,2-dimethyl-3-methylenecyclobutene mixed with a dimer of allene (yield 42%) and other minor products[120].

With typical dienophiles (acrylonitrile, azodicarboxylic ester) 1,1-difluoroallene forms a four-membered rings predominantly by means of the fluorinated double bond[7,106]. In the case of acrylonitrile[7] the proportions of isomeric products are 5:1:



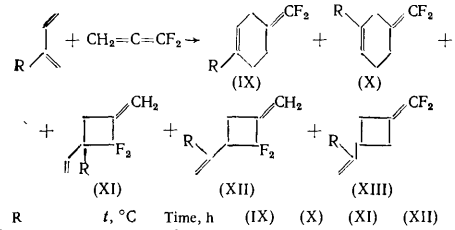
Halogenoallenes react quite well also with various 1,3-dienes, but in this case adducts of diene synthesis are formed primarily, together with 2,2-cycloaddition products[7,17,121]. The diene condensation has been reported of bromopropadiene[122], 1,1-difluoroallene[7,106], perchloroallene[17], trichlorobutadienoic acid[19], and 1,1-dichloro-3,3-bistrifluoromethylpropadiene[123] with cyclic dienes. These reactions always lead to the formation of only one of the isomers having an exocyclic halogenomethylene group



X, Y = H, Cl

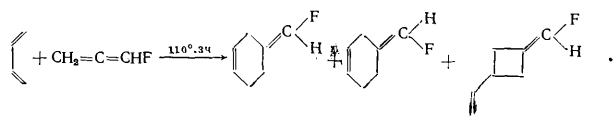
and may be of synthetic value for their preparation.

Table 2.



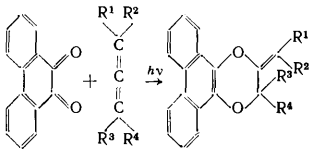
R	*t*, °C	Time, h	(IX)	(X)	(XI)	(XII)
R=H	110	7	63	—	37	—
R=CH_3	110	7.5	29	35	26	10
R=$(CH_3)_3SiO$	140	5.5	23	23	37	17

Addition of fluoroallene to butadiene forms a mixture of isomers at the *exo*-fluoromethylene group (yield 57%), the proportions of the reaction products being 2:2:1:[7]



Addition of 1,1-difluoroallene to alkylated dienes is still less selective: the yield of the adducts (IX) and (XIII) fluctuates between 60% and 90% (Table 2).[121] It is interesting that in both cases[7,121] an appreciable difference is observed in the addition of fluoroallenes: whereas 2,4-adducts are formed solely with an exocyclic mono- or di-fluoromethylene group, 2,2-adducts appear almost exclusively with an endocyclic difluoromethylene group; the proportions are (XI) + (XII) : (XIII) = 20 : 1.

Cycloaddition often occurs in photochemical processes. For example, 2,4-cycloaddition of 9,10-phenanthraquinone to dimethylbromoallene[124] leads to a roughly equally probable mixture of structural and geometrical cycloadducts of type (XIV: $R^1 = Br$, 9%; $R^2 = Br$, 7%; $R^4 = Br$, 13%):



(XIV)

When bromopropadiene is used under the same conditions[125], only one bond is involved in the reaction, with formation of a methylene-containing isomer (XIV: $R^1 = R^2 = R^3 = H$ and $R^4 = Br$).

Similarly, 4-chloro(and bromo)methylenetetramethyl-1-pyrazolines have been obtained (in respective yields 18% and 28%) from diazopropane and 1-chloro(and bromo)-3-methylbuta-1,2-dienes. The orientation in these examples corresponds to a hindered mode of cycloaddition[126,127].

The photoinduced addition of dehydrobenzene to chloroallene with formation of a chloromethylenebenzocyclobutane has been reported, but the yield is low (12%).[128]

3. Substitution of Halogen

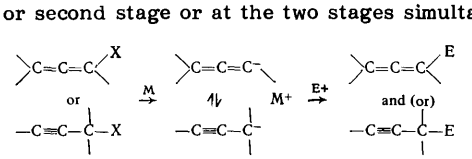
The ability of a halogen atom to be replaced by a nucleophilic species is directly dependent on the structure of the substrate. The presence of two electrophilic centres in a molecule is responsible for their peculiar reactivity, which depends in complicated fashion on the relative electrophilic properties of the centres, the nature of the nucleophilic, and solvolytic effects.

Subsequent discussions of α-halogenoallenes in nucleophilic reactions include consideration of parallel reactions of isomeric alkyne halides. This is necessary, since from the character of the changes they often lead to the formation of intermediate species that are resonance forms.

Reactions of halogenoallenes have been studied with water, alcohols, C–H acids, organometallic compounds, amines, metal hydrides, etc. The experimental results indicate that these reactions are governed by similar laws, and enable their most characteristic mechanisms to be examined.

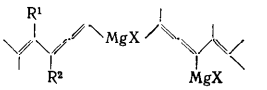
Organometallic derivatives

Halogenoallenes (and prop-2-ynyls) give with such metals as magnesium, zinc, aluminium, lithium, etc. organometallic derivatives, which then react with an electrophilic (E) with preservation and/or rearrangement of the initial molecule at the first or second stage or at the two stages simultaneously:



Reviews have recently appeared on this topic[129,130]. Not all the reactions have been discussed exhaustively, only the fundamental principles from the point of view of applying the especially valuable magnesium– and lithium–allene derivatives. It is considered at present that formation of Grignard reagents from halogenoallenes and the corresponding prop-2-ynyls is facilitated on the introduction of mercuric chloride or the addition of magnesium amalgam by the use of low temperatures (0–5 °C) and high-dilution technique[3,131,132].

1-Chloro- and 1-bromo-propadienes, as also the corresponding propynes, give with magnesium in ether a Grignard reagent, according to the infrared spectrum identical with the allene form but according to nuclear magnetic resonance data containing a greater proportion of the latter[3]. The preparation of α-deuteroallenylmagnesium bromide has been described[133]. Grignard reagents of vinylallenyl structure

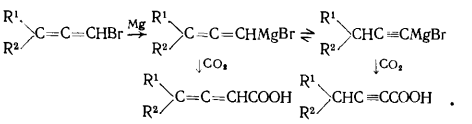


(XVa) (XVb)

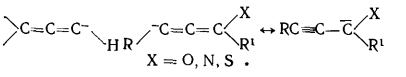
can be obtained by the action of magnesium on conjugated[129,134] and non-conjugated[135,136] vinylprop-2-ynyl halides. This method has wide application for the synthesis of diverse systems, in particular of phenomones and jasminoids[134–136].

Substitution of organo-magnesium and -zinc derivatives of allene in reactions involving electrophiles (water, aldehydes, ketones, epoxides, carbon dioxide, etc.) leads to their functionalisation. Attack takes place in general either at $C_{(1)}$ or at $C_{(3)}$. The regioselectivity of these reactions is ambiguous, and variations can be observed in the dependence on the nature of the metal (aluminium, magnesium, zinc)[137] and in the effects of various steric and electronic factors[138].

Sometimes competing side-reactions also lead to the formation of allene and/or acetylene derivatives. For example, hydrolysis of allenylmagnesium halides always occurs with partial formation of dimers of the hydrocarbon part of the initial halide[131,132]. Carbon dioxide gives exclusively or preponderantly allenic acids[43,48,49,131], the formation of acetylenic acids being explained by a slow prototropic shift in the allenylmagnesium bromide formed[131]:



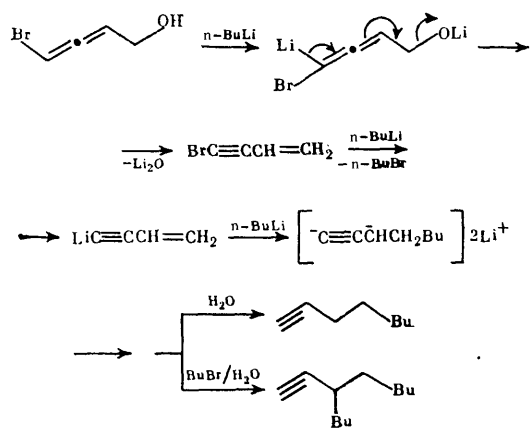
Lithiation of halogenoallenes gives good yields of lithium allenyls[59,139,140]; in many other cases the latter are generated by deprotonolysis[139–142], which occurs especially readily with hetero-substituted prop-2-ynyls:



In such reactions lithium reagents are especially attractive as synthons for organic synthesis. Reactions with diverse electrophiles clearly indicate the dual nature of the reagent, although in most cases they take place with retention of the allene structure[139–147].

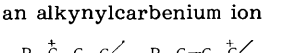
A curious rearrangement takes place in the action of butyl-lithium on 4-bromobuta-2,3-diene-1-ol. The reaction produces not only buta-2,3-dienol (in ~25% yield) but also a mixture of acetylenic hydrocarbons. An intermediate bromobutenyne is formed, which then reacts with butyl-lithium to form a dilithium prop-2-ynyl derivative that is converted into

the final hydrocarbons[148]:



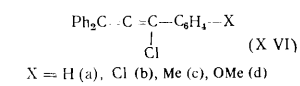
Hydrolysis (solvolysis) of allenyl halides

Allenyl halides, especially those containing electron-donor substituents in the α-position, tend to hydrolyse by an S_N1 mechanism via a cationoid allenyl intermediate, which is a resonance form of an alkynylcarbenium ion



The latter is formed also by heterolysis of the C–X bond in prop-2-ynyl substrates, and its structure has been reliably confirmed by the ^1H n.m.r. spectra of diarylalkynols in a strongly acid medium[149]. Jacobs and Fenton[52] were the first to suggest formation of an intermediate allenyl cation during hydrolysis.

Finally, a fairly recent study of the solvolysis of various triarylchloroallenes



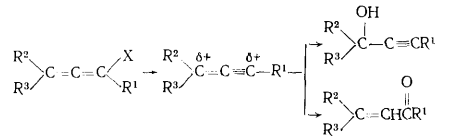
(XVI)

X = H (a), Cl (b), Me (c), OMe (d)

has shown that all these processes are unimolecular[54,150]. First-order kinetics has been established right up to 90% conversion, when reaction rates are independent of addition of a base. Solvolysis is characterised by a considerable accelerating effect of the ionic strength of the solvent [$m = 0.69$ and 0.77 for (XVIa) and (XVId) respectively] and a retarding effect of a salt having a common ion: the initial rate of solvolysis of triphenylchloroallene decreases by 29% in the presence of 0.1m lithium chloride[150]. The relative rates of reaction of the halogenoallenes (XVIa-d) in 80% aqueous acetone are 1 : 0.57 : 3.7 : 37.5. The element effect of the leaving group lies in the range $k_{Br}/k_{Cl} = 20$–58.

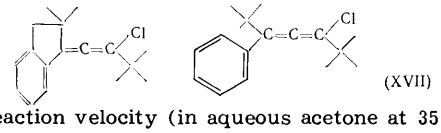
Similar rules have been illustrated by the solvolysis of a wide range of di- and tri-alkylated halogenoallenes with the alkyl groups in different positions (R^1, $R^2 = CH_3$, t-C_4H_9)[42,55]. The rate of solvolysis depends on the type and the number of substituents: on passing to bromopropadiene the rate constant decreases by a factor of 10^9.[151] The appearance of an element effect $k_{Br}/k_{Cl} = 20$–58, the reaction constant of arylated chloroallenes $\rho = -2.0$, and the entropy of activation of these reactions (−42 to +37 J mole^{-1} deg^{-1}) also agree well with substitution by an S_N1 mechanism.

In conformity with this the solvolysis of optically active 1-bromo-3-methylpenta-1,2-diene gives racemic products[152]. Finally, the effect of a salt on the observed solvolysis rate constant[152] and stereochemical data on recovery of the allenyl halide (complete retention of configuration)[153] indicate directly the possibility that the intimate ion-pair of the allenyl cation is involved in the transition state:



Substitution in allene derivatives by an S_N1 mechanism obeys different rules, since selectivity of attack is then determined by competition of the carbenium ion from two sides. The main products are acetylenic alcohols (yield 40–60%): i.e. preferential attack at the prop-2-ynyl centre of the cation is observed. Furthermore, addition takes place at the sterically less hindered carbenium centre, for unsaturated ketones are formed in the case of halogenoallenes having the substituents $R^2 = R^3 = t\text{-}C_4H_9$.[53,55]

An aromatic ring is more effective in influencing the rate of solvolysis when attached to $C_{(1)}$ than to $C_{(3)}$ (nine times as rapid)[55]. This is obviously due to the inability of such a ring at position 3 to attain a planar arrangement in order to act effectively on formation of a cationic centre and on its reactivity. It has been shown for the sterically fixed chloroallene



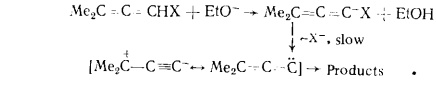
(XVII)

that the reaction velocity (in aqueous acetone at 35 °C) is higher than that of the open-chain analogue by a factor of 6800.[58]

An aromatic 3-substituent may be expected to have a greater influence in stabilising an allenyl than a vinyl cation. Stang[154] estimated this effect by comparing the reaction rate constants of triphenylallenyl and tri-p-methoxyphenylvinyl chlorides in 90% aqueous ethanol. The considerable kinetic effect of 10^6–10^9 in the rate constant can be explained by direct attachment of the aryl substituent to the carbon atom, which in a unimolecular process becomes a cation.

The influence of isotopes on reaction velocity has also been studied[42,155]. Replacement of α-hydrogen by deuterium in 1-bromo-3,4,4-trimethylpenta-1,2-diene lowers the rate, with an α-secondary isotope effect $k_H/k_D = 1.22$,[155] which far exceeds the usual isotope effect of hydrogen substitution in the solvolysis of alkyl bromides. Solvolysis of the above bromo-compound labelled with deuterium in the β′-position (CD_3) gave considerable secondary isotope effects (1.23). These results can be explained by additional stabilisation of the transition state and the intermediate carbenium ion by a greater contribution from the prop-2-ynyl structure.

The solvolysis of terminal halogeno allenes and prop-2-ynyl halides under conditions of catalysis by bases is of especial interest, since it enabled the possibility of substitution via an intermediate vinylidenecarbene—a zwitterion—to be demonstrated for the first time[156]. Mainly prop-2-ynyl substitution products are formed from a 3,3-dialkylated bromoallene:



There is no doubt about the mechanism of this reaction, at least in relation to the formation of vinylidenecarbene[157,158]. It is supported by physical and chemical tests: the reaction is not catalysed by bases when the acetylenic hydrogen is replaced by an alkyl group[159]; and the change in the activation volume indicates that water plays no part in the transition state. The positive but small activation volume

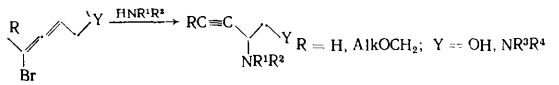
(+1.8 cm^3 $mole^{-1}$) is consistent with equally probable contributions by the two resonance structures[160].

From data on recovery of the allenyl halide (with the use of 1,4-disubstituted adamantanes as stereochemical label) it was concluded that a carbene–anion pair was involved in the reaction[153].

A carbene mechanism has been attributed to other reactions of halogenoallenes—with amines[156,161] C–H acids[162,163], Grignard reagents[164]—mainly by analogy with the mechanism of solvolysis. These reactions also take place in basic media, which favour carbene formation, e.g. under conditions of phase-transfer catalysis[165]. However, because of inadequate study of these reactions, there is no complete certainty that a carbene mechanism is involved.

Substitution by amines

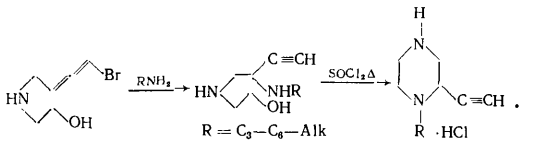
Replacement of halogen by an amine in a prop-2-ynyl halide is one of the most widely used methods for obtaining many aminoacetylenes, which show promise in research on physiologically active substances[166]. Halogenoallenes have been less investigated. It has proved possible to use these reactions, not with halogenoallenes themselves but with their functional derivatives. Examination of the reactions of allene bromides (I: R = H) and (III: R = AlkOCH$_2$)



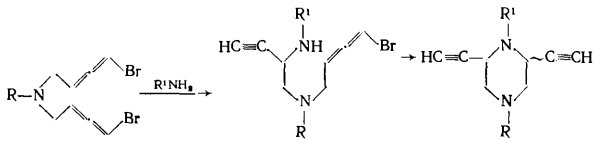
(I), (III)

with primary and secondary amines have shown that the sole process is replacement of the bromine atom by an amino-group. Substitution takes place at the γ-position, i.e. with simultaneous allene–acetylene rearrangement, to give vicinal difunctional acetylenes in ~40–70% yields[100,167,168].

Aminoalkylation also occurs with 1-bromo-4-2′-hydroxyethylaminobuta-1,2-diene[169]; although yields are not high, the resulting acetylenic diamino-alcohols can be converted by simple transformations into 2-ethynylpiperazines, which are difficultly accessibled by other means (yield ~30%):



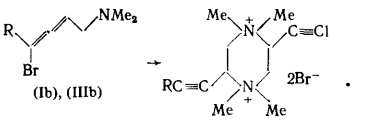
However, results for the heterocyclisation of *NN*-bis-4-bromobutadienylamines (II) are most interesting for preparative purposes; the only products are 2,6-diethynylpiperazines (an equimolecular mixture for *cis*- and *trans*-isomers) in 40–60% yield, apparently by intramolecular replacement of an atom in an intermediate diaminobromoallene[101,170]:



R=CH$_2$Ph, HOCH$_2$CH$_2$; R^1=C$_2$–C$_6$–Alk, CH$_2$Ph, 1-adamantyl .

This unusual, but smooth and obviously general reaction provides a good method for obtaining *C*-alkynyl derivatives of other heterocycles (nitrogen, oxygen, sulphur) and merits further study.

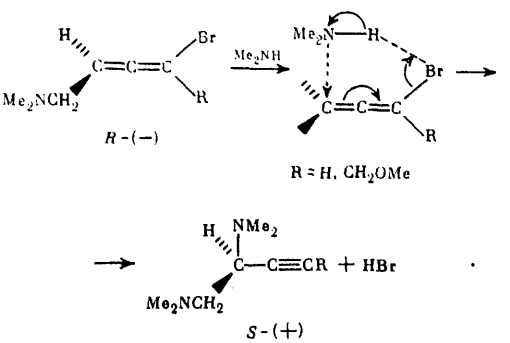
Finally, the dimerisation of bromo-*NN*-dimethylbuta-2,3-dienylamines (Ib, IIIb) (dimethylformamide at 20 °C) yields the corresponding salt of the quaternised 2,5-dialkynylpiperazine (which may be explained as both an intermolecular and an intramolecular process, in which a three-membered ring should be obtained)[170]:



(Ib), (IIIb)

The mechanism deserves special consideration. To elucidate the effect of the degree of substitution in the bromomethylene group on the direction, kinetics, and stereochemistry of substitution, two types of α-bromoallenes were used (Ib: R = H) and (IIIb: R = CH$_2$OCH$_2$). In the former case the reaction could occur via a carbene, and in the latter an allenyl cation could be formed. As noted above, the reaction is not complicated by secondary processes, gives the same regioselective substitution product in the two cases, and has overall second order (first with respect to the halogenoallene and first with respect to the amine)[171]. Even from these results it could be concluded that interaction with amines involves neither S_N1 alkylation nor a carbene stage.

Investigation of the stereochemistry of amino-substitution[172] involving optically active (–)-bromobuta-2,3-dienylamines (Ib) and (IIIb) has shown that the reaction with dimethylamine involves transfer of chirality with formation of (+)-acetylenic diamines†. Such constancy of structural, kinetic, and stereochemical relations indicates that the same type of transition state is involved in the two cases. From these facts a model of this complex was suggested with *cis*-orientation of entering and leaving groups, according to which aminoacetylenes should be formed with positive specific rotation for the *S*-configuration#:



Since the retroprop-2-ynyl rearrangement accompanying substitution involves essentially an S_Ni' mechanism, it is interesting that such reactions in the acyclic allyl system lead to predominance of the *cis*-isomer when the attacking nucleophile is neutral[173], and the *trans*-isomer if the nucleophile is ionic in character (RS^-).[174]

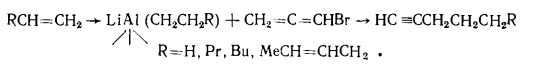
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† The degree of stereospecificity of the analogous reaction of (–)-(Ib) with (–)-α-methylbenzylamine is ≥80% (according to capillary gas–liquid chromatography)[170].

Erroneously termed an *R*-configuration in Ref. 172.

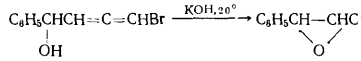
Other nucleophiles

Individual studies have been made of the conversion of allenyl halides in the Meyer reaction[175] with metal phosphides and arsenides[176] and with lithium tetrahydroaluminate[177], leading to the formation solely of acetylenic derivatives§. A novel method for obtaining terminal acetylenes (in 50–60% yield) is based on the hydroalumination of bromopropadiene[178]:

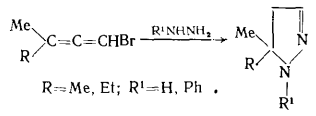


Under similar conditions prop-2-ynyl bromide yields terminal allenes[178].

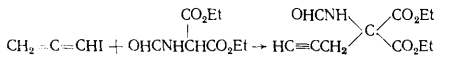
Halogen can be replaced by hydroxyl under suitable conditions[44,179]. A case has been reported of intramolecular substitution—rearrangement with formation of *trans*-2-ethynyl-3-phenyloxiran (yield 34%) from 4-bromo-1-phenylbuta-2,3-dien-1-ol in the presence of caustic potash[180]:



Substitution of dialkylallenyl bromides by hydrazines is accompanied by intramolecular cyclisation with formation of a 2-pyrazolines (yield 60–70%), reaction being facilitated by catalytic additions of copper(I)[181]:

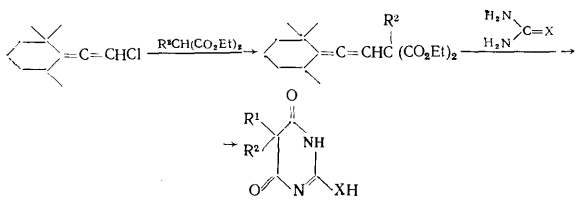


Compounds containing active hydrogen can be used. With acetoacetic ester halogenoallenes are assumed to undergo reactions having S_N2 and/or S_N2' mechanisms[182,183]. Under these conditions the isomeric 1-bromoallene and 3-bromopropyne give a moderate yield of a like mixture of mono and disubstitution products and cyclic compounds formed from them[182,183]. From iodoallene (mixed with 25% of 3-iodopropyne) with formamidomalonic ester in the presence of sodium ethoxide as base are formed the corresponding prop-2-ynyl derivatives in 67% yield[162]:



Similar reactions occur with alkylated halogenoallenes, but the proportion of isomeric allenic keto-esters[183] or diesters[162] increases with the steric hindrance of the halides.

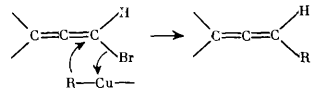
Similarly, alkylmalonic esters react with sterically hindered allenyl halides in the presence of sodium ethoxide to form allenic diesters, from which several allenic barbiturates (and thiobarbiturates) have been obtained by the action of urea (thiourea)[163]:



R^1 = t-BuCH = C = CH, t-BuC (Me) = C = CH, (iso-Pr)$_2$ C = C = CH, $Et_2C{=}C{=}CH$; R^2=Et, n-Bu; X=O, S .

§ Reactions of iodoallenes with vinyl cuprates have been used also for the synthesis of dehydroarachidonic acids[224].

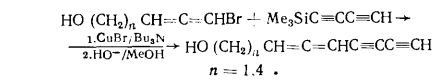
Halogenoallenes are converted by lithium dialkylcuprates[184,185] and copper cyanide[186] into allenic derivatives with replacement of the halogen via a four-centre transition state:



R = Alk, CN, $(AlkO)_2P(O)CH_2$.

The allenic structure is retained during cathodic reduction[187] and on reaction with lithium alkyls[188] and with a Grignard reagent in the presence of catalytic quantities of palladium chloride[189].

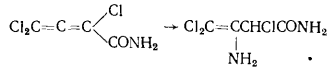
We note in conclusion that bromo- and iodo-allenes condense smoothly with terminal acetylene in the presence of copper salts and an amine (as a base) to form conjugated allene–acetylenes[67,190]. This process has been used to synthesise allene-diyne metabolites produced by micro-organisms[67]:



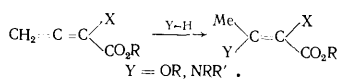
Under the influence of copper salts α-bromoallenes are converted into conjugated diallenes, the course of the reaction being strictly regioselective[191].

4. Linear Addition of Nucleophilic Reagents

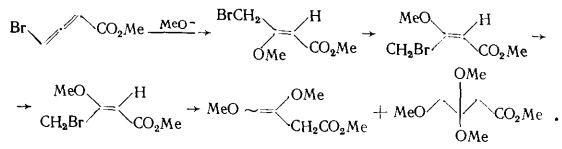
The allene group in α-halogeno-derivatives is usually resistant to attack by nucleophiles, and addition reactions have been little studied. Among them we may note firstly those of halogenoallenes containing electron-accepting substituents (alkoxycarbonyl, diethylphosphono, carbonyl). As might be expected, attack by the nucleophile (amine or alcohol) takes place exclusively at the carbon atom of the more electrophilic αβ-double bond, with formation of adducts corresponding to a protonated carbanion at the outer carbon atoms of the allene group. Adducts of crotonic type, being thermodynamically stable, may of course result also from prototropic isomerisation of vinylacetic adducts. 2,4,4-Trichlorobut-2,3-dienamide and ammonia form only the vinylacetic amino-derivative[26]:



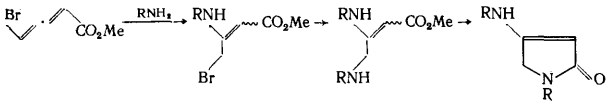
Primary and secondary amines and also alcohols (in the presence of an alkoxide) react smoothly with 2- [192] and 4-4-halogenobutadienoic esters[24,35,193] to give high yields of β-substituted derivatives of crotonic type:



However, involvement of γ-halogen in the reaction leads to formation of bisadducts. Thus mono-, di-, and tri-alkoxy-derivatives are formed with alcohols depending on the proportions of the components[193]: for the addition of methanol the reactions are

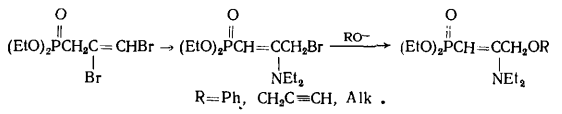


When excess of a primary amine is used, the resulting diaminocrotonic ester then undergoes cyclisation to form γ-alkylamino-substituted α-pyrrolinones, which cannot be obtained in other ways[35]:



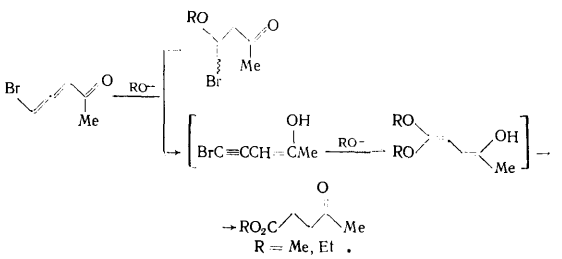
R=Et, n-Bu, t-Bu, CH_2Ph .

Several nucleophilic additions of amines and alcohols have been reported for βγ-dibromoalkenylphosphonates. The reactions involve an intermediate bromoallenylphosphonate. The method enables addition to be conducted selectively, and phosphonates to be synthesised to contain various functional substituents[21-23]:



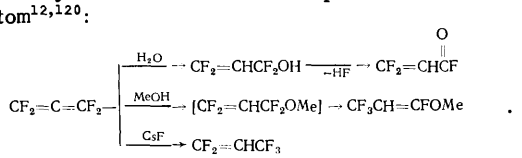
R=Ph, $CH_2C{\equiv}CH$, Alk .

The interaction of halogenoallenyl ketones with amines and alcohols has been studied considerably less. 5-Bromopenta-3,4-dien-2-one with alcohols gives only a small proportion of alkoxy-derivatives, the main reaction products being laevulinic esters. It is assumed that an intermediate ketenic acetal is formed by substitution at the *sp*-hybridised carbon atom[194]:



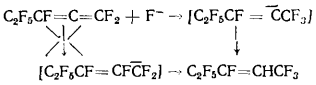
R = Me, Et .

Somewhat different rules are observed in the orientation of addition of nucleophilic reagents to perfluoroallene compounds, whose reactions have been widely studied. Tetrafluoroallene reacts with such reagents as water, methanol, and moist caesium fluoride under exceptionally mild conditions to give monoadducts. Elimination or rearrangement of the initial adducts can be observed at the same time, but the regioselectivity is such that the nucleophile adds to a terminal carbon atom[12,120]:

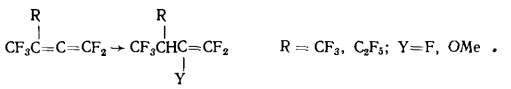


Similarly, perfluoropenta-1,2-diene gives monoadducts formed by attack at a terminal difluoromethylene group, with simultaneous formation of products of retroprop-2-ynyl rearrangement[195].

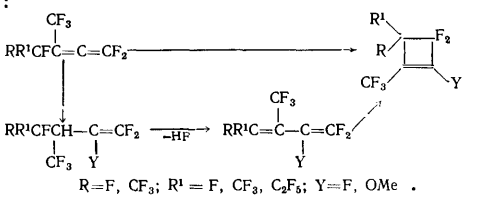
The orientation of nucleophilic addition to tetrafluoroallene and perfluoropenta-1,2-diene is directly opposite to that observed with halogenated buta-2,3-dienoic acids and related compounds discussed earlier. Such a course is not surprising, since attack by a nucleophile at the central carbon atom should produce an α-fluorocarbanion, which is unable to destabilise the positive charge on the fluorinated carbon atom[196]. In such cases only derivatives at a terminal carbon atom are formed: i.e. addition takes place at the double bond with formation of the most stable carbanion, stabilised by the perfluoroalkyl group:



Increasing the chain length of perfluoroalkyl-substituted allenes leads to a change in the orientation of addition. Their reactivity diminishes, but with increase in reaction time quantitative yields can be obtained even here[11]. The perfluorinated analogues of 1,1-methyl(alkyl)- and tetramethylallenes react with nucleophiles (methanol, caesium fluoride) to form monoadducts corresponding to regioselective attack at the central carbon atom[11,13,197]; hydrogen is directed solely to the end of the double bond substituted by the perfluoroalkyls:

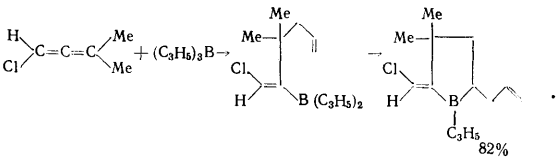


The monoadducts formed may undergo further changes, as e.g. in the reactions of 1,1-dialkylperfluoroallenes, when the resulting derivatives are dehydrofluorinated and spontaneously cyclised with high yields into the corresponding cyclobutenes[11]:



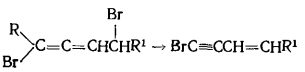
R=F, CF_3; R^1 = F, CF_3, C_2F_5; Y=F, OMe .

At 20 °C reaction takes place between triallylborane and dimethylchloroallene at the substituted double bond; the resulting diallylborane undergoes intramolecular cyclisation[198]:



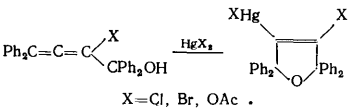
5. Other Reactions

Derivatised halogenoallenes exhibit specific properties towards several reagents in virtue of their structural features. Thus 1,4-dibromoallenes are sensitive to alkalis and readily undergo dehydrobromination involving the allyl bromine atom[90-92]:



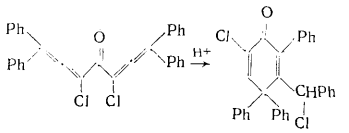
R=H, $SiMe_3$; R^1=H, Me, Et .

Treatment of halogenoallenes with acidic reagents[46,119,199,200] or with mercury salts[201] leads to unusual reactions, probably involving carbocation intermediates, which may be cyclised, depending on the presence of a functional group (hydroxy, phenyl), into derivatives of indene[46,119,201] or of dihydrofuran[199-201]:

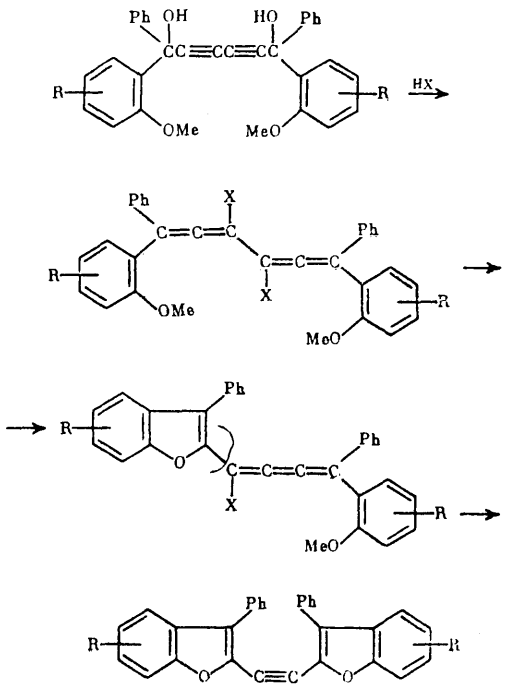


X=Cl, Br, OAc .

αβ-Unsaturated aldehydes and ketones are obtained under the same conditions[46,119,132]. Bis-3,3-diphenyl-1-chloroallenyl ketone is smoothly cyclised into cyclohexadienone in the presence of an acid[202]:

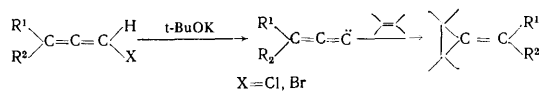


Symmetrical tetraphenylhexadiynediol under the influence of hydrogen halides undergoes two-stage cyclisation with formation of bisbenzofurylacetylenes[203]; study of this curious reaction showed the intermediate formation of a halogenobutatriene, which in the presence of activated alumina gives the final product in 35–45% yield:



R = H, Me, Cl, OMe; X = Cl, Br .

Under alkaline conditions halogenoallenes are able to eliminate a hydrogen halide containing the allenyl halogen atom. For example, heating bromoallenes with copper cyanide in dimethylformamide gives 45–65% yields of butenynes[39,204]. The most interesting is the 1,1-elimination of α-halogenoallenes. The method consists in acting on the latter with a strong base (usually potassium t-butoxide) with generation of a carbene; subsequent reactions with alkenes yield the corresponding cyclopropanes[205,206]:

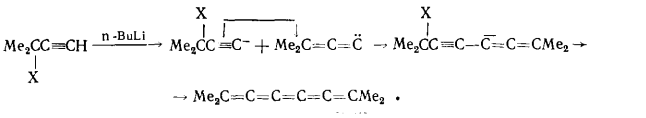


X = Cl, Br

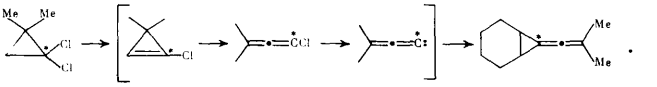
Better yields of carbene intermediates are observed if phase transfer is used in the presence of butyltriethylammonium chloride[165,166,207] or a crown ether[208,209].

Another method of generating carbenes consists in the intermediate formation of products of lithiation of halogenoacetylenes at the carbon-hydrogen bond. Under mild conditions isomerisation of the triple bond does not occur.

Above 25 °C, however, the lithium halogenoalkynides undergo unambiguous conversion into carbenes[210], which under the reaction conditions are often transformed into hetero-substituted (methylated, phenylated) hexapentaenes[47,211]:



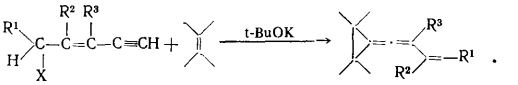
In a limited number of cases carbenes could be obtained from such compounds as 1,2-dibromo-3,3-diphenylallene (by the action of lithium alkyls[47]) and 3-alkyl-1-bromopropynes (by the action of alkoxides)[212,213]. The most interesting case was the preparation of dimethylvinylidenecarbene by the action of potassium t-butoxide (in Hexametapol) on dichlorocyclopropane (yield at most 6%), with intermediate formation of a chlorocyclopropene[214]:



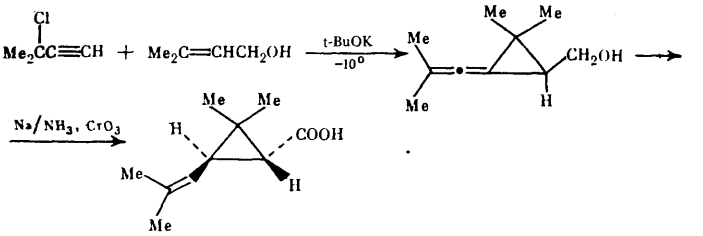
Such reactions constitute a special case, and can be used only for compounds analogous to those described above.

Towards alkenes allenylcarbenes behave as strong electrophiles, and undergo exclusively *cis*-addition, as has been demonstrated for dimethylvinylidenecarbene with *cis*- and *trans*-but-2-enes[209,215]. Study of the reactions of this carbene generated in different ways (from chloroprop-2-ynyl with potassium 2-butoxide or from bromoallene by the phase-transfer method) showed good agreement between the relative rate constants of the carbene with different alkenes[209].

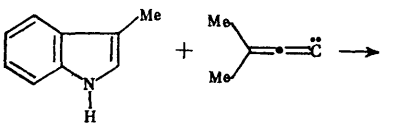
Various allenylcyclopropanes are readily formed, usually in satisfactory yield, also in the generation of allenylcarbenes from available halogenoprop-2-ynyl derivatives, which is of great value for their synthesis[216–218]. Analogous schemes are suitable also for the generation of vinylvinylidenecarbene[219]:

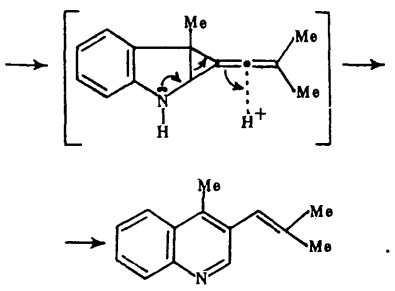


An interesting example is the stereospecific synthesis of *trans*-chrysanthemic acid by use of this carbene[220]:

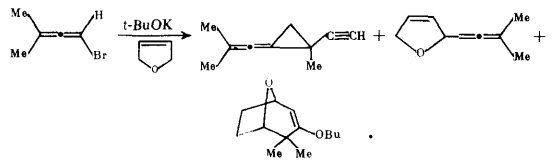


1-Bromoallenes react in basic medium (via the carbenes) with methylindoles to give alkynyl(allenyl)-3*H*-indoles[221] and alkenylquinolines—products of the ring expansion of allene intermediates:

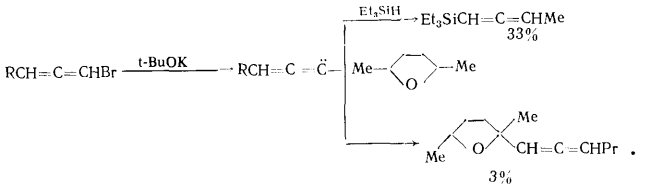




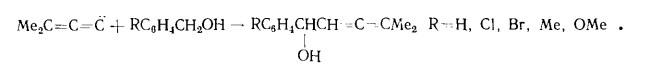
Dimethylvinylidenecarbene (generated from a halogenoallene by the action of potassium t-butoxide) reacts with dihydrofuran[222] to form, together with cyclopropanation products (yield 22%), also unsaturated compounds corresponding to incorporation of the carbene at a carbon-hydrogen bond:



The action of potassium t-butoxide on alkylallenyl bromides led to isolation of a carbene, which added to 2,5-dimethyloxolan and triethylsilane to give products involving incorporation at carbon-hydrogen and silicon-hydrogen bonds respectively[214]:



The action of dimethylvinylidenecarbene on alcohols (reaction between halogenoallenes and sodium ethoxide in alcoholic solution) usually gives satisfactory yields of products involving incorporation at a carbon–hydrogen bond, i.e. α-allenyl alcohols[223]:



---oOo---

As the above survey shows, α-halogenoallenes can be used to obtain many aliphatic, carbocylic, and heterocyclic functional derivatives belonging to various classes of organic compounds. Halogenoallenes can therefore be rightly regarded as effective and multipurpose starting materials for the synthesis of diverse compounds of theoretical and practical value.

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Protection of the Amino-group in Peptide Synthesis

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N-Protecting groups most widely used in peptides synthesis are examined. The possible mechanisms of the elimination of the protecting groups in acid and alkaline media are described and the methods of synthesis of the reactants for the introduction of certain protecting groups are considered.
The bibliography includes 65 references.

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I. INTRODUCTION

Two main trends may be isolated in the development of peptide chemistry: the improvement of methods for the formation of the peptide bond and the development of new more convenient protecting groups. The advances made in this field in recent times made it possible to simplify greatly the synthesis and to increase its effectiveness.

This review deals with the present state of the problem of the utilisation of *N*-protecting groups in the synthesis of peptides by the classical and solid-phase methods.

Despite the availability of deblocking methods such as catalytic hydrogenation, electrochemical reduction, treatment with sodium in liquid ammonia, irradiation with ultraviolet light, etc., the majority of protecting groups can be classified as either acid-labile or alkali-labile. Subsequently, we shall adhere to this conventional subdivision, considering other methods for the removal of protecting groups only in those cases where they are of special interest. The traditional protecting groups are described only briefly and some of these are not considered at all since their properties have been frequently discussed in the literature[1-5].

II. ACID-LABILE PROTECTING GROUPS

The first acid-labile protecting group, which has found extensive practical applications and which has exerted a great influence on the development of peptide synthesis, was the benzyloxycarbonyl group proposed in 1932 by Bergmann and Zervas[6]. The simplicity of the preparation and the ready availability of benzyloxycarbonyl derivatives, their high resistance to racemisation, and the wide variety of deblocking methods (treatment with hydrogen bromide in acetic acid, treatment with sodium in liquid ammonia, catalytic hydrogenolysis, and irradiation with ultraviolet light) are the main causes of the popularity of this protecting group.

New methods for the removal of the benzyloxycarbonyl protecting group, which have many advantages compared with the traditional methods, have been developed comparatively recently.

In 1977, Jackson and Johnstone[7] proposed a hydrogenation procedure involving hydrogen transfer, which proved convenient in the reduction of aromatic nitro-compounds. In the same year it was used to remove a number of protecting groups including the benzyloxycarbonyl group in classical peptide synthesis[8] and subsequently also in synthesis by the solid-phase method[9]. It was found that in this case the removal of the protecting groups is much faster and in addition it is possible to avoid the formation of side products in the deblocking of nitroarginine-containing peptides.

In the initial version, the hydrogenation with hydrogen transfer reduced to refluxing for several hours a solution of the protected derivative in ethanol in the presence of cyclohexene and palladium on charcoal or of palladium black. However, the refluxing of the peptide solution, which is itself undesirable, becomes particularly risky in the presence of protecting groups such as the t-butoxycarbonyl and t-butyl ester groups in view of the possibility of their being split off.

It has been shown[10] that these difficulties can be overcome when cyclohexa-1,4-diene is used as the hydrogen donor. In this case the deblocking is achieved at room temperature in 1.5–2 h in the presence of palladium and charcoal, while the use of palladium black permits the complete elimination of the protecting group in 5 min. The method proved convenient also for derivatives of certain sulphur-containing aminoacids, in particular methionine.

Yet another version of the hydrogenation reaction with hydrogen transfer was proposed in 1979, in which provision is made for the employment of formic acid as the hydrogen donor[11]. The benzyloxycarbonyl group is removed by treatment with a 4.4% solution of formic acid in methanol in the presence of palladium black in an atmosphere of nitrogen or by passing a solution of the protected derivative in methanol, containing 4.4% of formic acid, through a column containing palladium black. The time taken to eliminate the benzyloxycarbonyl group does not exceed 10 min in most cases; in addition this hydrogenation method greatly reduces the time taken to eliminate the *O*-benzyl groups.

Thus hydrogenation with hydrogen transfer makes it possible to remove rapidly and effectively the benzyloxycarbonyl group and a number of other protecting groups.

The t-butoxycarbonyl group, the parent of acid-labile groups eliminated under mild conditions, plays a no less important role in peptide synthesis. As a result of the appearance of this group[12], the possibilities of both the classical and solid-phase methods of synthesis of peptide have been greatly expanded.

Either the Schanabel method[13] or the Schwyzer method[14], in which the amino-group is acylated by treatment with the corresponding azide, were used initially to introduce the protecting group. However, in subsequent years a tendency arose to search for more efficient methods and reactants for the synthesis of protected derivatives. Here one may mention the application of systems such as t-butoxycarbonyl azide–triethylamine[15], t-butoxycarbonyl azide–imidazole, and t-butoxycarbonyl azide–1,1,3,3-tetramethylguanidine-1,2,4-triazole[16]. In the last case the method is so effective that it makes it possible to obtain fully protected derivatives of insulin by the direct acylation of the natural hormone, the yield of the reaction product exceeding 90%.

It has been suggested quite recently that the above protecting group be introduced using di-t-butyl pyrocarbonate[17]. The application of this reagent makes it possible to simplify greatly the method of synthesis and to increase the availability of the corresponding derivatives. Subsequent studies showed that the method is suitable also in the case of certain other protecting groups[18].

According to the method proposed by Pozdnev[17,18], the synthesis of aminoacid derivatives reduced to their treatment with di-t-butyl pyrocarbonate in the isopropyl alcohol–water system in the presence of triethylamine for 30 min at room temperature. The reaction takes place with a high yield (~90%) and the products formed do not as a rule require further purification.

Since the introduction of the t-butoxycarbonyl protecting group, the development of the solid-phase peptide synthesis has in essence begun. The employment of the benzyloxycarbonyl protecting group enabled Merrifield to synthesise only short model peptides[19] because of the occurrence of a side reaction involving the branching of the peptide–polymer bond in the deblocking process at acid pH. At the same time in the case of the t-butoxycarbonyl protecting group, under conditions ensuring its virtually quantitative removal, the degree of cleavage of the *C*-terminal benzyl ester is 1–2%.[20] As a result of this, it was possible to achieve the stepwise synthesis of ribonuclease A (124 aminoacid residues) by the solid-phase method[21].

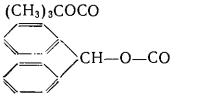
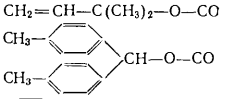
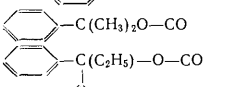
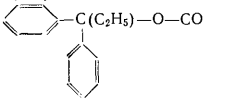
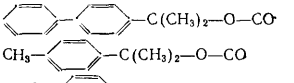
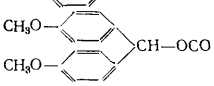
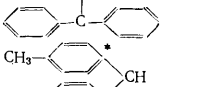
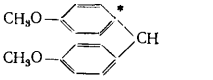
In the classical peptide synthesis the t-butoxycarbonyl protection of the α-amino-group in aminoacids is usually employed in combination with the following groups for the blocking of functional side groups in aminoacids: the nitro- or tosyl-group for the guanidino-group of arginine, the benzyloxycarbonyl group for the ε-amino-group of lysine, the benzyl group for the imidazole nitrogen of histidine and the sulphydryl group of cysteine, the benzyl ester groups for the carboxy-groups of glutamic and aspartic acid (and the *C*-terminal carboxy-group), and the benzyl ether groups for the hydroxy-groups of serine, threonine, and tyrosine.

Thus, after an appropriate choice of other protecting groups, the t-butoxycarbonyl group can be used successfully in the synthesis of peptides with a wide variety of aminoacid sequences by both classical and solid-phase methods.

Nevertheless, mention must be made of a series of specific difficulties arising in the employment of the protecting group. It is sufficient to note the problem of selectivity in the blocking of the α- and ε-amino-groups of lysine[22] and the t-butylation of the tryptophan-containing peptides, involving the removal of the t-butoxycarbonyl group[23–25]. It therefore became necessary to develop *N*-protecting groups more labile in acids than the t-butoxycarbonyl group and also groups which can be removed selectively in the presence of the t-butoxycarbonyl protecting group and the t-butyl ester groups used for the blocking of the functional side groups in aminoacids or the *C*-terminal carboxy-group.

The resistance of groups of this kind to the action of acids and the mechanisms of their elimination were investigated in detail in 1968.[26] It was shown in relation to various alkyl and urethane groups that the rate of their acidolytic cleavage depends on the stability of the carbonium ion formed and the acidity of the reaction medium. The rate of removal of certain protecting groups then proved to be 60000 times higher than that of the t-butoxycarbonyl group (Table 1). Unfortunately most of them are unsuitable for use in peptide synthesis owing to the instability of the azides or chloroformates used as the reagents for the introduction of the protecting group. The authors therefore decided to employ the diphenylisopropoxycarbonyl group[27], the rate of elimination of which is 3000 times higher than that of the t-butoxycarbonyl group. It has been suggested that this protecting group be introduced by the reaction of the corresponding azide or phenyl carbonate with aminoacid esters or salts. It proved possible to use dilute acetic acid and other weak acid reagents for the deblocking, which permits the retention of other acid-labile groups present in the growing peptide chain, particularly the t-butoxycarbonyl and t-butyl ester groups. By virtue of the large difference between the rates of elimination of the benzyloxycarbonyl and diphenylisopropoxycarbonyl protecting groups, it is then possible to solve the problem of selectivity for trifunctional aminoacids.

Table 1. The time of the 50% cleavage (τ_{50}) of $RHNCH_2COOY$ ($Y = C_2H_5$) with 80% CH_3COOH at 22–25 °C.[26]

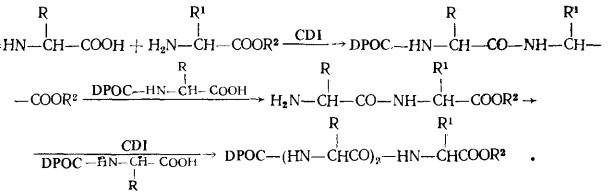
R	τ_{50}
$(CH_3)_3COCO$	58 days
	42 days
$CH_2=CH-C(CH_3)_2-O-CO$	14 h
	7 h
	2 h
	52 min
	30 min
	7 min
	1 min
	4 min
	28 days**
	~12 days

*Y = H.

**The degree of elimination was less than 0.1%.

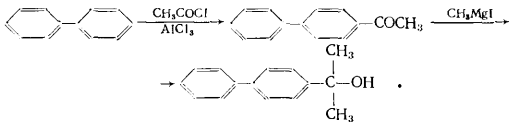
The disadvantages of the protecting group considered may include, together with the low availability of the initial reagents, also the unduly high acid lability, as a result of which the corresponding aminoacid derivative must be stored in the form of dicyclohexylammonium salts. Theoretically, there is even the possibility of removing the diphenylisopropoxycarbonyl (DPOC) protecting group in the course of the formation of the peptide bond under the influence of the COOH group of the carboxy-component[28], which can lead to the doubling of the aminoacid residue introduced in accordance

with the scheme†



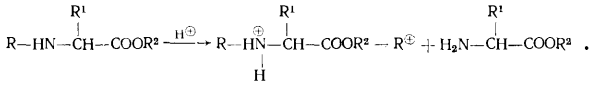
However, hitherto such cases have not been noted.

Since the diphenylisopropoxycarbonyl group is of undoubted interest from the standpoint of its employment in peptide synthesis, it is appropriate to consider the problem of the synthesis of the initial reagents for the introduction of this protecting group. In particular, the alcohol used as the starting compound in the synthesis of the corresponding azide or phenyl carbonate can be obtained as follows[29]:



We shall consider further the mechanism of the acid-catalysed elimination of alkyl and urethane protecting groups and the practical conclusions which follow from this.

In the case of alkyl groups, the cleavage under the influence of acids apparently proceeds via a mechanism involving the protonation of the nitrogen of the α-amino-group with the subsequent removal of the alkyl residue in the form of the corresponding carbonium ion:



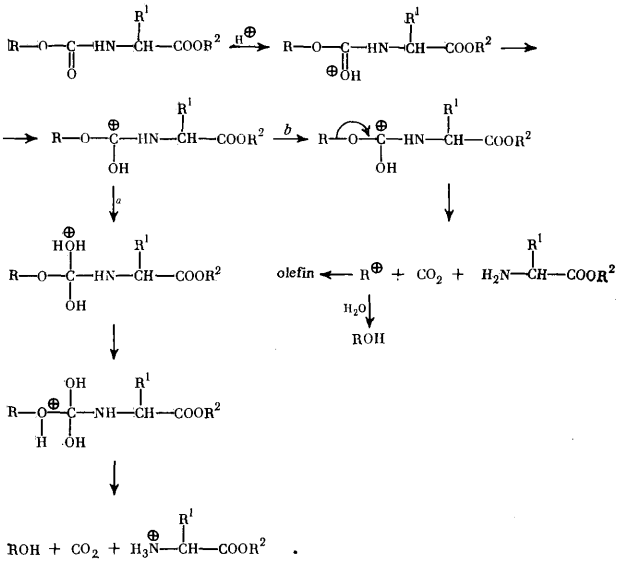
This is also indicated by the finding that, in the detritylation of peptides by treatment with an ethanol solution of hydrogen chloride under anhydrous conditions, ethyl trityl ether is formed in addition to the hydrochloride of the corresponding peptide, while in the presence of water triphenylmethanol is formed[30].

Evidently in this instance the rate of elimination of the protecting group is determined by the stability of the carbonium ion formed. Among the known groups of the type considered, the trityl group is therefore most readily removed by acids. Despite this, the trityl protecting group has not found extensive applications in peptide synthesis for the blocking of the α-amino-group owing to the steric hindrance which it generates and the associated difficulties in the synthesis of the corresponding derivatives. However, it is used to block the functional groups in the side chains of aminoacids (mainly the mercapto-groups of cysteine).

There is apparently a possibility of using protecting groups with a smaller number of phenyl moieties containing electron-donating substituents in the ring (Table 1), while the replacement of the phenyl moiety by the methyl moiety permits the stabilisation of the carbonium ion as a result of the formation of an olefin. However, one cannot rule out the possibility that in the latter case the problem may arise of the stability and reactivity of the halogeno-derivatives used for the introduction of such groups.

†CDI = dicyclohexylcarbodiimide.

In the acid cleavage of protecting groups of the urethane type, there is a possibility of two reaction mechanisms[31]. Structures related to the benzyloxycarbonyl group react via a bimolecular mechanism, while those related to the t-butoxycarbonyl group react via a unimolecular mechanism:



Hence it follows that groups of the first type are removed at a higher rate the greater the electron density in the benzene ring. Indeed, it has been shown[32] that the rate of cleavage of *para*-substituted derivatives of the benzyloxycarbonyl group by hydrogen bromide in acetic acid varies as follows:

$$CH_3O > C_6H_5 \sim CH_3 > H > F > Cl > NO_2 \quad .$$

In the case of groups of the second type there is a correlation between the rate of elimination of the protecting groups and the rate of solvolysis of the corresponding tosylates[33,34]. The results are presented in Table 2.

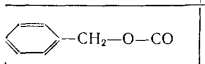
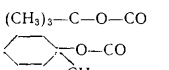
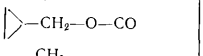
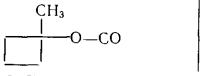
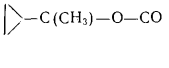
Their investigation enabled the authors[34] to propose a new protecting group—the 1-methylcyclobutoxycarbonyl group, which is stable in 50% acetic acid and is eliminated by treatment with trifluoroacetic acid in less than 30 min. The enhanced stability in relation to aqueous acetic acid, usually employed as the solvent in the purification of higher peptides, imparts to this group certain advantages compared with the t-butoxycarbonyl protecting group.

Comparison of the data in Tables 1 and 2 permits the following conclusions: (1) the rate of the acid-catalysed elimination increases sharply on passing from the bimolecular to the unimolecular mechanism; (2) the introduction of substituents promoting the delocalisation or decrease of the positive charge of the carbonium ion formed increases the rate of elimination; (3) the presence of a methyl group at the carbon atom with a positive charge also increases the rate of elimination as a result of the stabilisation of the carbonium ion by the formation of an olefin.

It is noteworthy that the formation of carbonium ions in the removal of protecting groups of the type considered is a source of extremely undesirable side reactions, such as the alkylation of the methionine and tryptophan residue[35], in the peptide synthesised. For example, Wünsch pointed out that deblocking with hydrogen fluoride in both classical and solid-phase synthesis favours the occurrence of side reactions

involving tryptophan derivatives even in the presence of added substances which reduce the extent of such reactions[36]. It has also been stated in a number of communications that the employment of additives such as mercaptoethanol, anisole, thioanisole, ethane-1,2-dithiol, scatole etc. by no means always guarantees the absence of side reactions[37-39].

Table 2. The 50% cleavage times (τ_{50}) of various *N*-protecting groups in the deblocking of phenylalanine derivatives[34].

Protecting group	τ_{50} (25° C, min)		Protecting group	τ_{50} (25° C, min)	
	CF_3COOH	HCOOH		CF_3COOH	HCOOH
	300	—		1*	4
	40	—		1*	2
	2	—		—	1.5

*Total cleavage time.

Returning now to the consideration of the acid-labile *N*-protecting groups, we shall consider those among them which have not found extensive applications in peptide synthesis but which may prove extremely valuable for this purpose by virtue of particular advantages.

Here we may mention in the first place the o-nitrobenzenesulphenyl protecting group[40], which has been used successfully in the synthesis of oxytocin analogues[41]. The corresponding protected derivatives are usually obtained with the aid of o-nitrobenzenesulphenyl chloride, although it has recently been suggested that *o*-nitrophenyl thiocyanate be used[42]. The latter is more stable on storage and reacts with aminoacids in the presence of silver nitrate at pH 6–9, giving rise to satisfactory yields. In 1979 Cipens and coworkers developed a new method for the synthesis of *o*-nitrobenzenesulphenyl chloride and *o*-nitrobenzenesulphenylaminoacids[43]. It was found that, when di-(2-nitrophenyl) sulphide is chlorinated with sulphuryl chloride in methylene chloride at 40–45 °C, it is possible to avoid the formation of impurities.

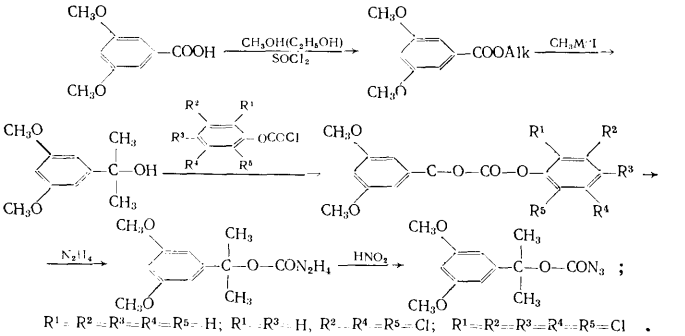
The *o*-nitrobenzenesulphenyl protecting group can be removed selectively in the presence of t-butyl esters with the aid of a solution of hydrogen chloride in diethyl ether.

It has been suggested[44] that the adamantyloxycarbonyl group be employed[44]. The protecting group is introduced with the aid of adamantyloxycarbonyl chloroformate, which can be obtained from the corresponding alcohol by treatment with an excess of phosgene in benzene solution in the presence of pyridine. The reaction with aminoacids takes place on cooling or at room temperature over a short period. The protecting group is removed by treatment with trifluoroacetic acid in the course of 15 min, adamantane forming a stable carbonium ion which can react with an anion from the surrounding medium but is incapable of losing a proton to form an olefin.

The authors[44] also noted that the adamantyloxycarbonyl derivatives are ninhydrin-positive on heating to 100 °C. It is likewise of interest that adamantyloxycarbonyl chloride can be used as the condensing agent in the synthesis by the method of mixed anhydrides, but this method of formation of the peptide bond is not of special value.

The t-pentyloxycarbonyl protecting group was proposed in 1967.[45] In contrast to the t-butoxycarbonyl group, the corresponding chloroformate could be used to introduce it. The reaction is carried out with the aminoacid ester and the resulting derivative is hydrolysed or converted into a hydrazide. t-Pentyloxycarbonyl azide or di-t-pentyl pyrocarbonate can also be used as the reagents for the introduction of the protecting group. The group hardly differs in its properties from the t-butoxycarbonyl protecting group.

The possibility of using the 3,5-dimethoxy-α,α-dimethylbenzyloxycarbonyl protecting group has been investigated[46]. Subsequently this group was used widely in the synthesis of peptides by both classical and solid-phase methods[47,48]. A method of synthesis of 3,5-dimethoxy-α,α-dimethylbenzyloxycarbonyl azide and the corresponding mixed phenyl carbonates from 3,5-dimethoxybenzoic acids via the following scheme has been developed (the yields are not less than 80% in all the stages):



These reagents are introduced into the reaction with aminoacid salts and Triton B in anhydrous pyridine. The protecting group can be removed selectively in the presence of the t-butoxycarbonyl group and t-butyl esters by treatment with 1–5% trifluoroacetic acid in methylene chloride for 8–30 min. It was found that the rates of the acidolytic elimination of the t-butoxycarbonyl, 3,5-dimethoxy-α,α-dimethylbenzyloxycarbonyl, and 2-(*p*-biphenylyl)isopropoxycarbonyl groups are in the ratios 1 : 1400 : 3000. The proposed protecting group is also photolabile, which makes it possible to remove it by ultraviolet radiation. The protected derivatives are thermolabile and give a positive response to the ninhydrin test on heating to 100 °C. The use of the above group in the synthesis by the method of mixed anhydrides makes it possible to simplify greatly all the operations and in addition to avoid the side reactions noted in a number of instances for proline-containing peptides[49].

Among the latest developments in the application of acid-labile *N*-protecting groups, mention may be made of the 1,1-(1-adamantyl)-1-methylethoxycarbonyl protecting group[50]. The phenyl carbonate synthesised from adamantane-1-carboxylic acid is used as the reagent for the introduction of this group. The reaction with aminoacids is carried out in dimethylformamide at 50 °C. The deblocking is achieved by treatment with 3% trifluoroacetic acid in methylene chloride for 2–3 min.

Other acid-labile *N*-protecting groups have either not found extensive applications in peptide synthesis or are of purely theoretical interest.

In conclusion it should be noted that the protecting groups eliminated under mild acid conditions play an important role in the classical and particularly in the solid-phase peptide synthesis. Their application for the protection of the *N*-end in the synthesis of polypeptides permits the employment for the blocking of the functional groups in the aminoacid side

chains not only of comparatively stable groups such as the benzyloxycarbonyl groups but also of groups of the type of t-butoxycarbonyl and t-butyl esters. This simplifies both the operations in the course of the growing of the peptide chain and the deblocking stages.

III. ALKALI-LABILE PROTECTING GROUPS

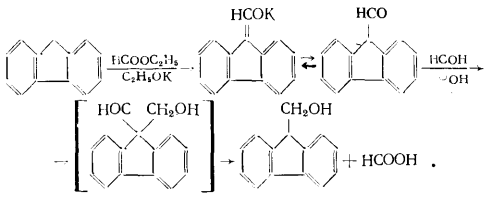
It is noteworthy that at the present time only a few alkali-labile groups of this type are used in peptide synthesis. However, the results show that the search for protecting groups eliminated under mild alkaline conditions constitutes an extremely promising development in peptide chemistry. Indeed, the appearance of such protecting groups would make it possible to avoid the difficulties arising in deblocking by acids of methionine- and tryptophan-containing peptides and their use in combination with the acid-labile protection for the functional groups in the side groups of aminoacids would greatly extend the scope of peptide synthesis.

The first step in this direction was the use of the trifluoroacetyl protecting group[51]. Trifluoroacetylaminoacids can be obtained by treating the aminoacid with trifluoroacetic anhydride in anhydrous trifluoroacetic acid or by the aminolysis of trifluoroacetate esters, while the protecting group can be eliminated by treatment with aqueous ammonia, sodium hydroxide, or barium hydroxide or by interaction with basic ion-exchange resins.

Unfortunately there is a possibility of a whole series of side reactions even in the course of the formation of the protected aminoacid derivatives and in addition under certain conditions rearrangements are observed with formation of azlactones, which leads to the racemisation of the protected aminoacid residue. Trifluoroacetyl derivatives are therefore used mainly only in gas-chromatographic analysis for the determination of the aminoacid sequence or of the degree of racemisation[52,53].

The 9-fluorenylmethoxycarbonyl protecting group, developed in 1970, is nowadays used to an increasing extent in peptide synthesis[54]. The authors introduced this group by means of the corresponding azide or chloroformate in aqueous dioxan in the presence of sodium bicarbonate or carbonate.

The starting compound for the synthesis of the reagents used to introduce the above protecting group is 9-fluorenylmethanol. The latter is a comparatively inaccessible compound but it can be readily obtained from fluorene in accordance with the following scheme[62]:



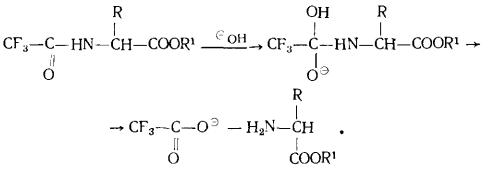
The yield of the final product was more than 67%. The intermediate 9-formylfluorene need not apparently be isolated in a pure form.

The protected aminoacids or peptides are deblocked by treatment with liquid ammonia, ethanolamine, morpholine, or similar bases. It has recently been suggested that piperidine bound to polystyrene[55] or other polymeric bases[56] be used for this purpose. According to Carpino and Han[54], the 9-fluorenylmethoxycarbonyl group is stable under the conditions where it is treated with hydrogen bromide or chloride in organic solvents and trifluoroacetic acid and also under hydrogenolysis conditions. However, a special study of the hydrogenation of protected derivatives in methanol in the presence of small amounts of acetic acid and 10% of palladium on charcoal showed that the side products are formed in this instance[57]. The authors explained the observed discrepancy in the results by the different qualities of the catalysts employed: a partially poisoned catalyst can be inactive in relation to the derivative considered.

In the classical peptide synthesis the 9-fluorenylmethoxycarbonyl protecting group has been used in the successive growing of the peptide chain by the method of activated esters[58] and also for the blocking of the α-amino-group in trifunctional aminoacids in combination with the t-butoxycarbonyl group and the t-butyl ester[59] groups for the protection of the functional side groups. Side reactions, leading to the dimerisation of the aminoacid residue introduced, have been noted in a few instances under these conditions.

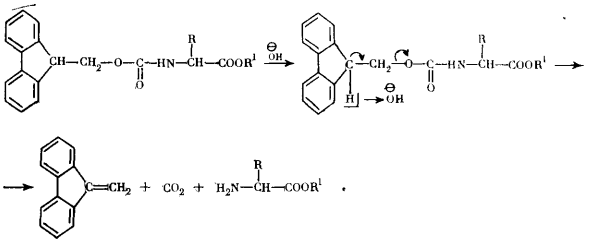
The possibilities for the employment of the derivatives under consideration in the solid-phase peptide synthesis have been investigated in detail[60,61].

In the study of the mechanisms of the elimination of alkali-labile groups, certain formal analogies can be drawn with the mechanisms of the elimination of the acid-labile protecting groups. Thus protecting groups related to the trifluoroacetyl group are removed in accordance with the following scheme:



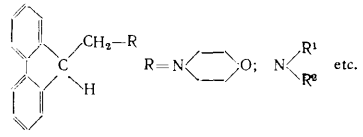
The above reaction equation resembles formally the acid-catalysed elimination of an alkyl group and in both cases the protecting group is removed without fragmentation and with formation of the corresponding ion. In the instance considered the reaction rate is evidently determined by the fractional positive charge on the carbon atom of the carbonyl group.

Unique ideas concerning the mechanism of the removal of the 9-fluorenylmethoxycarbonyl protecting group have not so far been developed. The nature of the solvent is apparently significant in this instance. In aprotic solvents the process mechanism has not been established, while in water, methanol, and t-butyl alcohol it is close to the carbanionic mechanism[56]. To a first approximation, the elimination of the 9-fluorenylmethoxycarbonyl group can be represented by the equation



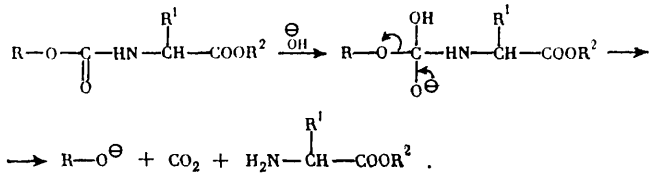
The character of this reaction is similar to that of the elimination of protecting groups of the benzyloxycarbonyl type—the group fragments in both instances and the process is not

accompanied by the formation of ions having an independent existence. In this instance the rate of cleavage is determined by the stability of the intermediate carbanion. The stabilisation of the carbanion derived from the 9-fluorenylmethoxycarbonyl protecting group is achieved by β-elimination, leading to the formation of dibenzofulvene. Depending on the reaction conditions and the reagents used in deblocking, an adduct with dibenzofulvene of the type



can be formed as a side product.

Continuing the comparison of the mechanisms of the elimination of the acid- and alkali-labile protecting groups, one may postulate the existence of a third pathway leading to the removal of the alkali-labile groups. The reaction must then proceed via a fragmentation stage with formation of independently existing ions, as happens in the case of the t-butoxycarbonyl group. The mechanism of this process can be represented by the equation



Evidently the rate of this reaction depends on the stability of the anion formed and hence on the electronic effects of the substituent R. The possibility of the operation of this mechanism is confirmed indirectly by the finding that, on passing from the benzyloxycarbonyl group to the phenoxy- and naphthoxy-carbonyl and related protecting groups, which might show a greater tendency towards the formation of anions on fragmentation, an increase of resistance to the action of hydrogen bromide in acetic acid is observed. The elimination under the influence of this reagent can be carried out only under severe conditions leading to the rupture of the peptide bond[63]. Apparently the introduction into the benzene ring of substituents promoting the stabilisation of the anion formed would make it possible to obtain alkali-labile protecting groups of the type considered. At the present time such *N*-protecting groups are not used in peptide synthesis.

A number of studies devoted to the search for new alkali-labile protecting groups and to the expansion of the applications of the already existing groups have been published in recent years. As early as 1970, the possibility of modifying the 9-fluorenylmethoxycarbonyl group in order to increase or decrease its sensitivity to bases was pointed out[54].

In 1978 Merrifield suggested that the 2-sulpho-9-fluorenylmethoxycarbonyl protecting group be used in the elimination of side products with a shortened aminoacid sequence from the peptides synthesised by the solid-phase method[64]. The 2-sulpho-9-fluorenylmethoxycarbonyl group is attached to the amino-group of the peptidylpolymer and the resulting derivative and other elimination products are separated on diethylaminoethyl-cellulose and deblocked. The protecting group is introduced using the corresponding chloroformate or the *p*-nitrophenyl ester of the aminoacid. The deblocking is carried out by treatment with aqueous morpholine or piperidine.

The possibility of using the *p*-substituted benzyloxycarbonyl group as an alkali-labile protecting group has been investigated recently[65]:

$$R-COO-C_6H_3(R^1)-CH_2-OCO-$$

$R = CH_3$, $R^1 = H$; $R = (CH_3)_2CH$, $R^1 = H$; $R = OC_2H_5$, $R^1 = H$; $R = (CH_3)_2CH-O$, $R^1 = H$; $R = C_2H_5S$, $R^1 = H$; $R = (CH_3)_2CH-NH$; $R^1 = H$; $R = (CH_3)_2N$, $R^1 = H$; $R = (CH_3)_2CH-O$, $R^1 = Cl$.

It was shown that groups of this type are more stable in trifluoroacetic acid than the benzyloxycarbonyl protecting group and can be removed selectively in the presence of the latter and the t-butoxycarbonyl group by treatment with H_2O_2 in ammonia.

Thus, despite the fact that the use of alkali-labile *N*-protecting groups in peptide synthesis is so far still fairly limited, the data obtained hitherto show that this trend will have a significant influence on its development.

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Phosphorus Acid Azides

V.A.Gilyarov

Data on the synthesis and the chemical and physical properties of phosphorus acid azides are surveyed. The bibliography includes 100 references.

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I. INTRODUCTION

Although the first phosphorus acid azides (PAA) were described in 1953,[1,2] the bulk of the studies on their synthesis and their properties have been carried out during the last 15–20 years. The synthesis of PAA has been greatly developed and the ready availability and in the vast majority of cases also the high stability of these compounds have been demonstrated, which constitutes their advantageous features compared with other azides, for example, aryl azides.

The chemical properties of PAA are very close to those of aryl, alkyl, and sulphonyl azides. PAA readily undergo the Staudinger reaction. Interaction of PAA with phosphorus(III) derivatives has led to the full availability of a new class of phosphorimido-compounds–substances containing the $\rangle P{=}N{-}P(X)\langle$ group, where X = O or S. The photolysis of PAA results in the formation of nitrenes capable of various reactions; in particular, in certain cases the groups attached to the phosphorus atom migrate to the nitrogen atom, i.e. a reaction analogous to the Curtius reaction takes place. PAA add to unsaturated compounds. On the other hand, the azide group in PAA exhibits the properties of a pseudohalogen and is capable of being substituted by other groups in reactions with nucleophiles. The study of the chemical properties of PAA established detailed differences between them and other azides, for example, sulphonyl azides. Thus, in terms of the number of reactions, PAA occupy one of the first places among phosphorus acid derivatives.

Recently one of the PAA, namely diphenyl phosphorazidate (diphenyl azidophosphate), has found extensive applications in organic synthesis, the synthesis of peptides, alkyl azides, etc.

There are a few reviews on PAA.[3–5] The first review[3] deals only with azides with a phosphorus–carbon bond. The last review[5] is the most complete but it covers the literature only up to 1973. The fundamental monographs[6,7] on organophosphorus compounds deal only briefly with PAA. It therefore became necessary to write the present review, which deals with the PAA synthesis, indicating the methods of synthesis, the yields, and the constants.

II. SYNTHESIS

The principal method of synthesising PAA involves the replacement of the chlorine atom in the corresponding chlorides by the azide group. The methods based on the employment of phosphorus acid anhydrides and hydrazides have been developed only slightly.

1. Synthesis from Phosphorus Acid Chlorides

Metal azides (principally sodium azide and more rarely lithium azide) or organoelemental azides in which the azide group is partly mobile (trimethylsilyl azide or PAA) are used to substitute the chlorine atom in phosphorus acid chlorides:

$$(RO)_2P(O)Cl + MN_3 \rightarrow (RO)_2P(O)N_3 + MCl,$$
$$(RO)_2P(S)Cl + MN_3 \rightarrow (RO)_2P(S)N_3 + MCl.$$

Various solvents have been proposed for sodium azide: acetone[1,8–10] (method *a*), pyridine[11–14] (method *b*), acetonitrile[9,15] (method *c*), DMF [16] (method *d*), water[2] (method *e*), ethanol[17] (method *f*), and methylene chloride[18] (method *g*). The reaction with lithium azide is carried out without a solvent[19], in acetonitrile[20,21] (method *h*), or in tetrahydrofuran (THF) [22] (method *i*). The most general method of synthesis of PAA proved to be the reaction with a concentrated solution of triethylammonium azide in chloroform[23,24] (method *j*). Tables 1–7 present the PAA synthesised with an indication of the method of synthesis, the yield, and the constants.

Table 1. Phosphorus(III) acid azides.

Formula	Method of synthesis	Yield, %	B.p., °C (mmHg)	M.p., °C	Refs.
$P(N_3)_3$	*c*	97	—	—	[25]
$[(iso\text{-}C_3H_7)_2]_2PN_3$	—	81	65–67 (0.01)	37–39	[26]
$(CF_3)_2PN_3$	—	—	—60 (1)	—	[19]
$(C_6H_5)_2PN_3$	*h*	—	—	13.6–13.8 (decomp.)	[20]

In the synthesis of diphenylphosphinic azide (I), the influence of the solvent on the rate of exchange of the chlorine atom was investigated:

$$(C_6H_5)_2P(O)Cl + NaN_3 \xrightarrow{\sim 20^\circ} (C_6H_5)_2P(O)N_3 + NaCl$$
(I)

The rate of reaction increases in the sequence benzene << dioxan < THF << pyridine[11].

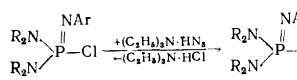
Method (a). Phosphorus acid chlorides react with sodium azide in acetone at room temperature or on prolonged refluxing. It cannot be claimed that the method is universal; for

example, when it is employed, the chlorine atom in dibutylphosphinic chloride is incompletely substituted by the azide group[23].

Method (b). Pyridine is the most universal solvent for the synthesis of PAA. The completion of the reaction can be monitored by analysis for chlorine. The advantages of this method are the mild reaction conditions (the reactants are stirred at room temperature) and the comparative ease of isolating the PAA. A possible side reaction involves the alkylation of pyridine by the PAA containing the RO groups (particularly in the case of the lower esters), which makes it necessary to limit contact between the reaction product and pyridine. Limitations to the method have also been found: in the case of *N,N,N',N'*,tetra-alkyl-*N''*-arylphosphoroamidimdic chlorides it is impossible to achieve a complete substitution of the chlorine atom by the azide group[52]. Apparently the accumulation of nitrogen atoms at the phosphorus atom and the associated extensive delocalisation of the effective positive charge significantly reduce the capacity of the halogen for substitution.

Method (d). The use of dimethylformamide (DMF) proved to be convenient in the synthesis of dialkyl phosphorazidothioates[16]. However, the PAA obtained must not be soluble in aqueous DMF (at the end of the reaction the mixture is diluted with water and the PAA is extracted with an organic solvent). It is noteworthy that, when an attempt was made to synthesise diarylphosphinic azides by this method, negative results were obtained[12].

Method (j). As already mentioned, this is the most universal method. Indeed its employment makes it possible to obtain PAA (for example, compounds 1, 2, and 3 in Table 6) from acid chlorides in which the chlorine atom is relatively inert.



Triethylammonium azide may prove useful in the synthesis of other PAA, which are difficult to obtain by other methods. The lack of side reactions, the complete substitution of chlorine in the acid chlorides by the azide group, and the mild reaction conditions are undoubted advantages of this method.

When *N,N'*-dialkylphosphorodiamidic chlorides were treated with lithium azide in acetonitrile at 50 °C, *N,N'*-dialkylphosphorodiamidic azides (II) were obtained in a low yield, decomposition being observed on boiling the solution[37]:

$$(RNH)_2P(O)Cl \xrightarrow[CH_3CN]{LiN_3} (RNH)_2P(O)N_3\ (II)\ .$$

The employment of sodium azide in aqueous acetone also gives rise to a low yield of the azide (II).

2. Synthesis from Phosphorylpyrazoles

Certain PAA have been obtained from phosphorylpyrazoles in which the P–N bond is of the anhydride type[43]:



R=R'=OCH$_3$; R=OCH$_3$, R'=C$_6$H$_5$.

3. Synthesis from Phosphorus Acid Anhydrides

The reactions of phosphorus acid anhydrides with sodium azide, leading to the formation of PAA, can be illustrated schematically as follows[57]:

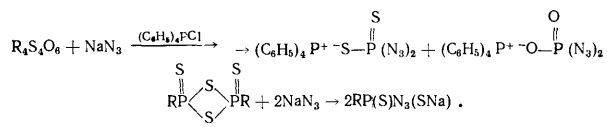


Table 2. Phosphoric acid azides.

Formula	Method of synthesis	Yield, %	B.p., °C (mmHg) or m.p., °C	n_D^{20}	d_4^{20}	Refs.
$(N_3)_3PO$	*c*	98	—	—	—	[25]
$CH_3OP(O)(N_3)_2$	*c*	87	—	—	—	[27]
$(CH_3)_2NP(O)(N_3)_2$	*c*	60	—	—	—	[27]
$CH_3OP(O)(ONa)N_3$	—	—	146—148	—	—	[28]
(t-C$_4$H$_9$—C$_6$H$_3$—OP(O)(OH)N$_3$	*a, e*	—	221—225 (decomp.)	—	—	[29]
$(CH_3O)_2P(O)N_3$	*e**	35	79.5—81 (10)	1.4276	1.3013	[30]
$(C_2H_5O)_2P(O)N_3$	*a*	62.8	76—77 (4.5)	1.4260	1.1672	[30]
$(C_3H_7O)_2P(O)N_3$	*i*	90.5	64 (025)	1.4367	1.1029	[23]
$(iso\text{-}C_3H_7O)_2P(O)N_3$	*j*	92.4	62—64 (2)	1.4265	1.0824	[23]
$(C_4H_9O)_2P(O)N_3$	*j*	75.4	86—87 (0.5)	1.4372	1.0713	[23]
$(iso\text{-}C_4H_9O)_2P(O)N_3$	*b*	76	66.5 (0.2)	1.4325	1.0528	[31]
$(s\text{-}C_4H_9O)_2P(O)N_3$	*b*	68	54—55 (0.03)	1.4322	1.0592	[31]
(t-C$_4$H$_9$—C$_6$H$_4$—O)$_2$P(O)N$_3$	—	—	44—47	—	—	[29]
$(C_6H_5O)_2P(O)N_3$	*a*	90	157 (0.17)	—	—	[32]
$RO(C_6H_5NH)P(O)N_3$ (R = 2-adamantyl)	*a, e*	39	oil	—	—	[33]
$p\text{-}ClC_6H_4O(RHN)P(O)N_3$ (R = 1-adamantyl)	—	59	112—114	—	—	[33]
t-C$_4$H$_9$—C$_6$H$_3$—OP(O)(NHC$_6$H$_5$)N$_3$	*a, e*	49	93—95	—	—	[29]
CH$_3$, C$_3$H$_7$-iso—C$_6$H$_2$—OP(O)(NHC$_6$H$_5$)N$_3$	*a, e*	—	146—150	—	—	[29]
$[(CH_3)_2N]_2P(O)N_3$	*b***	75	93—94 (2)	1.4673 (21°)	—	[17]
$([CH_3)_2N]_2P(O)N_3 \cdot SbCl_5$	—	31	116	—	—	[34]
$[(C_2H_5)_2N]_2P(O)N_3$	*b*	88	76 (0.01)	2.4670	1.0504	[35]
$[CH_3(C_6H_5)N]_2P(O)N_3$	*a, e*	89	—	—	—	[34]
$(C_6H_5CH_2NH)_2P(O)N_3$	*a****	40	65—67	—	—	[36]
$(C_6H_{11}NH)_2P(O)N_3$	*a, e*	30	64—66 and 94—96	—	—	[36]
$(C_6H_5NH)_2P(O)N_3$	*c*	30	90—95			
$[CH_2(CH_2)_3N]P(O)N_3$	*a, e*	64	—	—	—	[36]
$[CH_2(CH_2)_3N](C_6H_5NH)P(O)N_3$	*a, e*	36	—	—		[37]
$[(CH_3)_2N]_2P(OCH_3)N_3^+SbCl_6^-$	—	35	141			[38]
$P(N_3)_5$	*c*	97	—	—	—	[25]

*The yield obtained by method *c* is 65%.
**The yield obtained by method *c* is 78.5%.
***The yield of the synthesis from $(C_6H_5CH_2NH)_2P(O)NHNH_2$ is 10%. [36]

Table 3. Phosphorothioic acid azides.

Formula	Method of synthesis	Yield, %	B.p., °C (mmHg) or m.p., °C	n_D^{20}	d_4^{20}	Refs.
$(CH_3O)_2P(S)N_3$	*a*	51	38—39 (0.5)	—	—	[1]
$(C_2H_5O)_2P(S)N_3$	*a*	—	60 (1.5)	—	—	[1]
$[n\text{-}C_3H_7O)_2P(S)N_3$	*d*	58	57—58 (1)	1.4720	1.1659	[16]
$(iso\text{-}C_3H_7)_2P(S)N_3$	*a*	—	77—78 (1)	—	—	[1]
$(C_4H_9O)_2P(S)N_3$	*d*	64	84—85 (6)	1.4630	1.0707	[16]
$(uзо\text{-}C_4H_9O)_2P(S)N_3$	*d*	65	88—89 (0.2)	1.4699	1.0789	[16]
$(C_6H_5O)_2P(S)N_3$	*d*	56	67—70 (0.2)	1.4699	1.0789	
$[(CH_3)_2N]_2P(S)N_3$	*d*	35	25—27	—	—	[16]
$[(C_2H_5)_2N]_2P(S)N_3$	*b*	75	80 (1.5)	1.5177 (21)	—	[17]
S, S, O$_2$P$_2$S$_2$, N$_3$	*a, e*	91	177—178	—	—	[38]

Table 4. The azides of methyl- and phenyl-phosphonic and methyl- and phenyl-phosphonothioic acids.

Formula	Method of synthesis	Yield, %	B.p., °C (mmHg) or m.p., °C	n_D^{20}	d_4^{20}	Refs.
$CH_3P(O)(OC_2H_5)N_3$	*j*	78	39(0.1)	1.4480	1.1926	[39]
	b	63	36—37(1.5)	1.4460	1.1882	[31]
$CH_3P(O)(OC_6H_5)N_3$	*j*	92	80(0.04)	1.6289	1.2559	[39]
$ClCH_2P(O)(OC_2H_5)N_3$	*j*	84	74—75(0.05)	1.4750	1.3478	[39]
$ClCH_2P(O)(OC_6H_5)N_3$	*j*	74	117—118(0.06)	1.5420	1.3662	[39]
$CH_3P(O)(SC_2H_5)N_3$	*e*	43	78—79(1—2)	1.5190	1.2507	[40]
$CH_3P(O)[N(C_2H_5)_2]N_3$	—	80	76—77(0.03)	1.4680	1.0891	[41]
$CH_3P(O)(NH_2H_5)N_3$	—	99	—	1.5740	—	[41]
$CH_3P(O)(NHCOOCH_3)N_3$	—	66	82—83	—	—	[41]
$CH_3P(O)(NHCOOC_2H_5)N_3$	—	77	127—128	—	—	[42]
$CH_3P(O)(NHCOOC_3H_7\text{-iso})N_3$	—	77	114—115	—	—	[42]
$CH_3P(O)(NHCOOC_6H_5)N_3$	—	70	96—98	—	—	[41]
$CH_3P(O)(NHCONHC_6H_5)N_3$	—	—	158—166 (decomp.)	—	—	[42]
$CH_3P(O)(NHCONC_6H_4Cl\text{-}n)N_3$	—	—	164—166 (decomp.)	—	—	[42]
$CH_3P(O)(NCO)N_3$	—	52	49—50(0.04)	1.4835	1.3975	[41]
$CH_3P(O)(Cl)N_3$	*b*	67	46—47(0.03)	1.4850	1.4125	[41]
$CH_3P(O)(N_3)_2$	*b*	52	49—50(0.03)	1.4980	1.3826	[41]
$C_6H_5P(O)(OCH_3)N_3$	—	36*	95(0.01)	—	—	[43]
$C_6H_5P(O)[N(CH_3)_2]N_3$	*b*	—	86—88(0.001)	1.5473	—	[14]
$C_6H_5P(O)[N{=}P(C_6H_5)_3]N_3$	—	—	143—145	—	—	[14]
$C_6H_5P(O)(Cl)N_3$	—	—	66—67(0.75)	1.5636		[14]
$CH_3P(S)(OC_2H_5)N_3$	*b*	60.5	60(8)	1.4960	1.1572	[31]
$C_6H_5P(S)(N_3)_2$	*b*	—	—	—	—	[14]

*For the method of synthesis, see Section III, 1.

Table 5. The azides of phosphinic, phosphinothioic, and phosphinoselenoic acids.

Formula	Method of synthesis	Yield, %	B.p., °C (mmHg) or m.p., °C	n_D^{20}	d_4^{20}	Refs.
$(CH_3)_2P(O)N_3$	*b*	69	46—48(1); 14—16	—	—	[44]
$(CD_3)_2P(O)N_3$	*b*	74	48(1)	—	—	[45, 46]
$CH_3(C_2H_5)P(O)N_3$	*b*	—	32(10^{-2})	—	—	[45]
$CH_3(C_6H_5)P(O)N_3$	*b*	100	65(0.3)	—	—	[13, 45]
$(C_2H_5)_2P(O)N_3$	*b*	—	97(8)	—	—	[47]
$(C_2H_5)_2P(O)N_3$	*b*	85	97(8)	—	—	[44]
$(C_4H_9)_2P(O)N_3$	*b, c*	61	95(7)	—	—	[48]
$C_2H_5(C_6H_5)P(O)N_3$	*b*	—	—	—	—	[45]
$(iso\text{-}C_3H_7)_2P(O)N_3\cdot 0{,}15H_2O$	*b, d*	74	72—78(0.5)	—	—	[48]
$(C_4H_9)_2P(O)N_3$	*j*	40.9	78—79(0.2)	1.4648	1.0102	[23]
$(t\text{-}C_4H_9)_2P(O)N_3\cdot 0{,}35H_2O$	*b, d*	80	75—80(0.5)	—	—	[48]
$(CH_3)_2CCH(CH_3)C(CH_3)_2P(O)N_3$	*b*	65	80—82(0.2)	—	—	[49]
$CH_2C(CH_3)_2C(CH_3)_2P(O)N_3$	*d*	—	81(0.4)	—	—	[49]
$(CH_3)_2CCH_2C(CH_3)_2P(O)N_3$	*d*	81	95—100(2.5)	—	—	[49]
$(C_6H_5)_2P(O)N_3$	*b*	87	137—140 (0.05)	1.6077	1.23	[12]
$(C_6H_5)_2P(O)N_3$	*j*	74.3	95(10^{-4})	1.6080	1.2374	[23]
$(p\text{-}CH_3C_6H_4)_2P(O)N_3$	*b*	—	190—195(0.5)	—	—	[12]
$(p\text{-}ClC_6H_4)_2P(O)N_3$	*b*	—	160—165 (0.05)	1.6246	—	[12]
$B_{10}H_{10}C_2(C_6H_5PN_3)_2$	*f*	82	126—128	—	—	[50]
$B_{10}H_{10}C_2PN_3)_2$	*f*	81	150 (разл.)	—	—	[50]
$B_{10}H_{12}[(C_6H_5)_2PN_3]_2$	*f*	96	147	—	—	[51]
$(CH_3)_2P(S)N_3$	*a*	73	69—70	—	—	[44, 45]
$(CD_3)_2P(S)N_3$	*a*	95	72	—	—	[45, 46]
$CH_3(C_2H_5)P(S)N_3$	*a*	90.5	37—38(10^{-2})	—	—	[45]
$CH_3(C_6H_5)P(S)N_3$	*a*	—	—	—	—	[45]
$(C_2H_5)_2P(S)N_3$	*a*	87	70—71(1)	—	—	[44]
$C_2H_5(C_6H_5)P(S)N_3$	*a*	—	—	—	—	[45]
$(C_6H_5)_2P(S)N_3$	*b*	87.4	137—140 (0.05)	—	—	[12]
$(CH_3)_2P(Se)N_3$	*a*	71	69—70	—	—	[45, 46]
$CH_3(C_2H_5)P(Se)N_3$	*a*	50	47—48(10^{-2})	—	—	[45]
$CH_3(C_6H_5)P(Se)N_3$	*a*	—	—	—	—	[45]
$(C_2H_5)_2P(Se)N_3$	*a*	71	69—70	—	—	[45, 46]
$C_2H_5(C_6H_5)P(Se)N_3$	—	—	—	—	—	[45]
$(C_6H_5)_2P(Se)N_3$	*b*	45	25	—	—	[45, 46]

4. Synthesis from Phosphorus Acid Hydrazides

The azides (II) have been obtained in a very low yield by the reaction of *N,N'*-dialkylphosphorodiamidic hydrazides with nitrous acid:

$$(RNH)_2P(O)NHNH_2 + HNO_2 \rightarrow (RNH)_2P(O)N_3 + 2H_2O \quad .$$
(II)

The use of the above reaction has not been extensively developed for the synthesis of PAA. Although the employment of dialkyl phosphorohydrazidothioates for the synthesis of dialkyl phosphorazidothioates has been described[58], methods *a* and *d* (from dialkyl phosphorochloridothioates) proved to be more convenient for their synthesis:

$$(RO)_2P(S)NHNH_2 + HNO_2 \rightarrow (RO)_2P(S)N_3 + 2H_2O \ ;$$
$$R = CH_3,\ C_2H_5,\ C_3H_7 \ .$$

When methyl hydrogen phosphorohydrazidate $CH_3OP(O).(NHNH_2)OH$ was treated with nitrous acid, only the evolution of nitrogen was observed; the expected azide $CH_3OP(O)(N_3).OH$ could not be obtained under these conditions[28].

Table 6. The azides of phosphorodiamidimidic and phosphinimidic acids.

№	Formula	Method of synthesis	Yield, %	B.p., °C (mmHg) or m.p., °C	n_D^{20}	d_4^{20}	Refs.
1	$[(CH_3)_2N]_2P(=NC_6H_5)N_3$	*j*	64.2	88—89(0.04)	1.5580	1.1270	[52]
2	$[(C_2H_5)_2N]_2P(=NC_6H_5)N_3$	*j*	60	72—74(10^{-4})	1.5390	1.0622	[52]
3	$[(C_2H_5)_2N]_2P(=NC_6H_4CH_3\text{-}p)N_3$	*j*	66	80—81(10^{-4})	1.5370	1.0511	[52]
4	$(C_6H_5)_2P(=NC_6H_5)N_3$	*i*	83	—	—	—	[22]
5	$(C_6H_5)_2P(=NSO_2C_6H_4CH_3\text{-}p)N_3$	*g*	76	84—85	—	—	[22]

5. Synthesis of Triazidophosphine and Phosphoric Triazide

The possibility of the formation of $P(N_3)_3$ and $PO(N_3)_3$ by the reaction of PCl_3 and $POCl_3$ with ammonium azide in liquid sulphur dioxide and the extremely high risk of their exploding were noted in the first communication[4] on the synthesis of these PAA. When $POCl_3$ is treated with ammonium azide in liquid SO_2 at −30 °C, a crystalline product is formed, but explodes when an attempt is made to isolate it.

In a later study[25] $P(N_3)_3$ and $PO(N_3)_3$ were obtained by the reaction of PCl_3 and $POCl_3$ with sodium azide in acetonitrile at −20 °C. After separating the precipitate by evaporating the filtrate at 0 °C, the azides were obtained in the form of readily hydrolysable liquids, which frequently explode on being heated to room temperature.

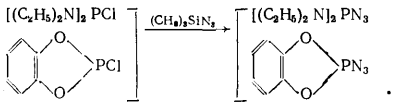
Table 7. The azides of cyclic λ^5-phosphazenes.

Formula	Method of synthesis	Yield, %	B.p., °C (mmHg) or m.p., °C	Refs.
$2,2\text{-}(H_2N)_2N_3P_3(N_3)_4\text{-}4,4,6,6$	*e*	—	81—82	[53]
$N_3P_3(C_6H_5)_5N_3$	—	—	153.5—155	[54]
$N_3P_3F_5N_3$	*a*	95	53(77)	[55]
$N_3P_3(N_3)_6$	*a, e*	~100	<−20	[56]
$N_4P_4F_7N_3$	*a*	65	54(40)	[55]

6. Phosphorus(III) Acid Azides

The azides of tervalent phosphorus acids are difficult to obtain. For this reason, the number of azides of this type isolated hitherto is small (Table 1). The azides are apparently formed readily from the corresponding chlorides and sodium azide or trimethylsilyl azide. The main cause of the difficulty of their isolation is their high reactivity, which

leads to the formation of cyclic and linear phosphonitriles as a result of self-condensation. Thus the use of trimethylsilyl azide in the reaction with chlorodiphenylphosphine under various conditions (variable temperature and solvents) did not yield azidodiphenylphosphine, but invariably led to the formation of its further transformation products[59]. The syntheses of the following azides are merely mentioned in the literature: $[(CH_3)_2N]_2PN_3$,[26] $(t\text{-}C_4H_9)_2PN_3$,[26] $\{[(CH_3)_3Si]_2N\}_2.PN_3$,[60] and $(C_6F_5)_2PN_3$.[61] Azidobis(diethylamino)phosphine[62] and *o*-phenylene phosphorazidite[63] were obtained in accordance with the following scheme:



These azides are stable only below 10–15 °C. The products of the self-condensation of *o*-phenylene phosphorazidite were obtained by the reaction of *o*-phenylene phosphorochlorodite with trimethylsilyl azide at 80 °C.[64]

III. CHEMICAL PROPERTIES

Two groups of reactions with participation of the azide group are most characteristic of PAA: reactions with phosphorus(III) compounds leading to the evolution of nitrogen, the formation of compounds with the fragment $\geq P=N-P(X)\leq$ (X = O or S) and the reaction in which the azide group reacts as a pseudohalogen (phosphorylation). Other reactions of PAA are noteworthy—pyrolysis, photolysis, and addition to unsaturated systems.

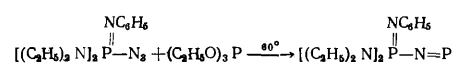
1. Reactions of PAA with Phosphorus(III) Compounds

The reactions of PAA with tervalent phosphorus compounds constitute an extension of the Staudinger reaction to PAA:

$$(RO)_2P(O)N_3 + (R'O)_3P \rightarrow (RO)_2P(O)N{=}P(OR')_3 + N_2 .$$

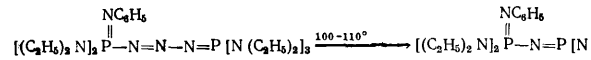
These reactions are general and, when the azide and the phosphorus(III) compounds are varied, many classes of phosphorimido-compounds, a considerable proportion of which cannot be synthesised by the Kirsanov reaction, can be obtained.

The rate of reaction depends on the structure of the reactants—of both the azide and the phosphorus(III) compound. Special kinetic studies of the influence of substituents in the azide molecule have still not been made, but it is known that *N,N,N',N'*-tetra-alkylphosphorodiamidic azides react with phosphorus(III) compounds more slowly than dialkyl phosphorazidates[35]. *N,N,N',N'*-Tetra-alkyl-*N''*-arylphosphorodiamidimidic azides react with particularly great difficulty, for example[52]:



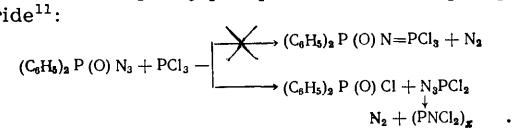
Azidobis(diethylamino)phosphine does not react with triethyl phosphite[63].

The mechanism of the reactions of PAA with phosphorus(III) compounds has not been investigated. By analogy with other azides (aryl azides and sulphonyl azides), the reaction presumably proceeds via triazenes, which decompose with evolution of nitrogen. The triazene has been isolated in only one instance and its heat treatment led to the formation of a phosphorimido-compound[52]:



The structure of the triazene was not investigated; the proposed structure is analogous to that of the triazenes formed from aryl and sulphonyl azides. A somewhat reduced (compared with aryl azides) reactivity in the reactions of PAA with phosphorus(III) compounds is noteworthy. In the case of PAA, the reaction are usually carried out at 50–60 °C,[31] while aryl azides react even at room temperature.

If the phosphorus(III) chloride is an acid chloride (phosphorus trichloride, chlorodiphenylphosphine), then the azide group is exchanged for the halogen in the reaction with PAA.[11,21] Thus a phosphonitrilic chloride polymer is formed in the reaction of diphenylphosphinic azide with phosphorus trichloride[11]:

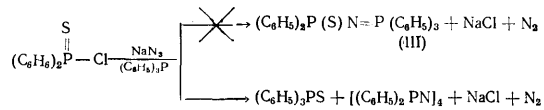


An analogous reaction is possible also in the case of chlorodiphenylphosphine[21]:

$$(I) + (C_6H_5)_2PCl \rightarrow (C_6H_5)_2PN_3 + (C_6H_5)_2P(O)Cl .$$

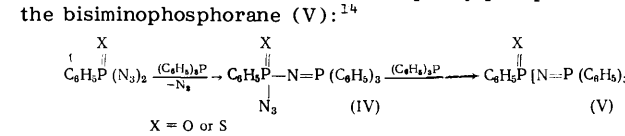
The main product proved to be $(C_6H_5)_2P(O)[N=P(C_6H_5)_2]_2Cl$ (yield 60%), whose formation can be represented as the result of a series of consecutive reactions of the azide (I) with $(C_6H_5)_2PN_3$ followed by the exchange of the N_3 group for Cl.

The reaction of diphenylphosphinothioic chloride with sodium azide and triphenylphosphine led to the isolation of the tetramer of diphenylphosphonitrile instead of the expected *N*-(diphenylphosphinothioylimino-*p,p,p*-triphenylphosphorane(III):[11]



Diphenylphosphinothioic chloride is apparently initially converted into chlorodiphenylphosphine, which then reacts with sodium azide.

In the presence of two azide groups in the PAA a stepwise reaction with triphenylphosphine is possible. Thus the azide (IV) can react further with triphenylphosphine to form the bisiminophosphorane (V):[14]

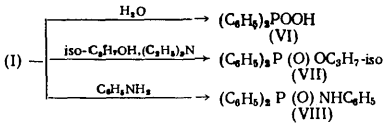


The reactions of various PAA with a wide variety of phosphorus(III) compounds, namely triphenylphosphine[11,14], the bisphosphines $(C_6H_5)_2P-X-P(C_6H_5)_2$ (X = *p*-C_6H_4 or *p*-$C_6H_4C_6H_4$-*p*),[14] alkyl dialkylphosphinites[23], dialkyl phosphonites[23], trialkyl phosphites[16,30,31], dialkyl phosphoramidites[31,35], alkyl phosphorodiamidites[35], and phosphorous triamides[31,35]. The reactions of PAA with trialkyl phosphorothioites have not been described.

2. Reactions of PAA involving the Azide Group as a Pseudohalogen

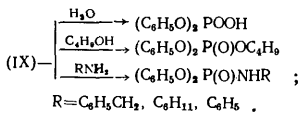
In the reactions of diphenylphosphinic azide with nucleophiles (water[11], isopropyl alcohol[11], and aniline[11,65]), its azide group is substituted with formation of diphenylphosphinic acid (VI), isopropyl diphenylphosphinate (VII),

and diphenylphosphinic anilide (VIII):



N-(Azidophenylphosphinylimino)-*p*,*p*,*p*-triphenylphosphorane $(C_6H_5)_3P{=}NP(O)(C_6H_5)N_3$,[14] diphenyl phosphorazidate (IX),[66] and diethyl phosphorazidate $(C_2H_5O)_2P(O)N_3$ (X) [8] are capable of undergoing similar reactions involving the substitution of the azide group.

Comparison of the reactivities of the last two azides in reactions with nucleophiles permits the conclusion that the mobility of the azide group in the azide (IX) is much greater than in the azide (X). The azide (IX) interacts with water and butanol on boiling. The azide (IX) reacts with aliphatic amines with self-heating, while the reaction with aniline is terminated after 3 h on refluxing in alcohol[66]:

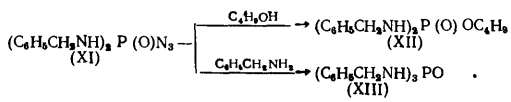


Diethyl phosphorazidate reacts with aniline under severe conditions (17.6 h at 185 °C). *N*-Phenylphosphoramidic acid $(HO)_2P(O)NC_6H_5$ was then isolated, evidently as a result of a secondary reaction involving the alkylation of aniline by the diethyl *N*-phenylphosphoramidate formed. Indeed, diethyl *N*-phenylphosphoramidate is rapidly converted into this acid on being refluxed in aniline[8].

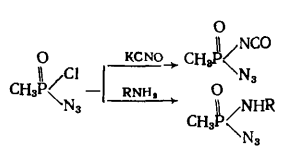
The solvolysis of diethylphosphinic azide in methanol takes place comparatively readily, while sterically hindered azides (di-isopropyl- and di-t-butylphosphinic azides) do not react with methanol in the course of 17 h at room temperature[48].

Although solutions of diaryl phosphorazidates in pyridine are readily hydrolysed by water in pyridine, the pure azides are hydrolysed only slowly in 0.5 *N* NaOH. The resistance of PAA to hydrolysis is noteworthy. It makes it possible to obtain them in an aqueous medium (method *e*). The ready hydrolysability of dimethyl phosphorazidothioate has been noted[44]. The kinetics of the hydrolysis and ammonolysis (in reactions with butylamine and benzylamine) of methyl phosphorazidate have been investigated. The formation of the corresponding phosphoramidates in this process has been demonstrated[28].

The azide group in phosphorodiamidic azides is more resistant to the action of nucleophiles. Thus *N*,*N*′-dibenzylphosphodiamidic azide (XI) reacts with butanol and benzylamine under severe conditions (for example, refluxing in butanol for 18 h), forming the ester (XII) and the triamide (XIII) respectively[36]:



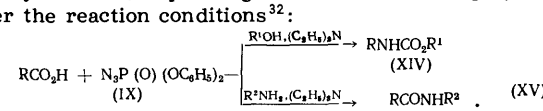
The azide group is less reactive than the chlorine atom in nucleophilic substitution reactions[42]:



PAA are more resistant to hydrolysis than the corresponding acid chlorides[44].

The reaction of the azide group as a pseudohalogen constitutes the basis of the modification of the Curtius reaction with participation of the readily available diphenyl phosphorazidate; this reaction has found extensive applications recently. Diethyl phosphorazidate was used initially[67], but the azide (IX) gave better results.

Thus the urethane (XIV) or the amide (XV) is formed from carboxylic acids, depending on the reactants employed under the reaction conditions[32]:



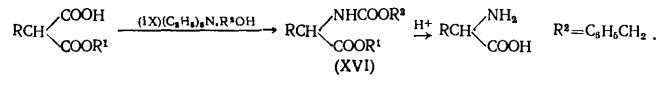
The urethanes (XIV) are obtained by refluxing equimolar amounts of a carboxylic acid, triethylamine, and the azide (IX) in the presence of a hydroxy-compound. This modification of the Curtius reaction† proved successful, since it is carried out under more or less neutral conditions and in the absence of oxidants (highly alkaline or acid media of the kind necessary for the Hofmann or Schmidt reactions are not required). In addition, it is possible to employ acids which do not enter into the Schmidt reaction (for example, pyridine-2-carboxylic acid). Table 8 presents certain results of the application of the azide (IX) in the syntheses of urethanes.

Table 8. The modified Curtius reaction involving the use of diphenyl phosphorazidate (R^1CH = t-C_4H_9OH).[68]

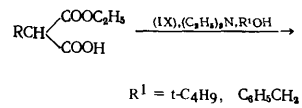
RCO_2H	Reaction time, h	Reaction product	Yield, %
$C_6H_5CH_2CO_2H$ *	20	$C_6H_5CH_2NHCO_2C_2H_5$	51**
$C_6H_5CH_2CH_2CO_2H$	25	$C_6H_5CH_2CH_2NHCO_2C_4H_9$-t	61
		C_6H_5—$CH_2CH_2NHCON_3$	3
$C_6H_5CH{=}CHCO_2H$	5	$C_6H_5CH{=}CHNHCO_2C_4H_9$-t	70
α-$HO_2CC_5H_4N$	23	α-{t-C_4H_9OCONH}C_5H_4N	73
p-$NO_2C_6H_4CO_2H$	20	*p*-$NO_2C_6H_4NHCO_2C_4H_9$-t	84
o-$NO_2C_6H_4CO_2H$	15	*o*-$NO_2C_6H_4NHCO_2C_4H_9$-t	90
$C_6H_5CO_2H$	21.5	$C_6H_5NHCO_2C_4H_9$-t	44
		$C_6H_5NHCON_3$	16
		$(C_6H_5NH)_2CO$	14

*R^1OH = C_2H_5OH.
**Diethyl phosphorazidate was used.

The attempt to convert the monoester of malonic acid into an aminoacid made it possible to obtain the ester (XVI) only when benzyl alcohol was used[69] and the latter must be added after refluxing a mixture of the azide (IX) and triethylamine for 1 h:



When a mixture of acid, the azide (IX), triethylamine, and alcohol is refluxed, the esters (XVII) are formed invariably[69,70]:

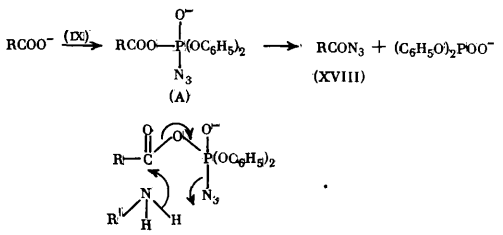


R^1 = t-C_4H_9, $C_6H_5CH_2$.

†The reaction under consideration is in a certain sense similar to the Schmidt reaction, but, from the standpoint of the mechanism (see below), the authors[68] regard it as a "modification of the Curtius reaction".

The mechanism of the reactions of substituted malonic acid monoesters with the azide (IX) and alcohols has been investigated and a scheme has been proposed whereby one can account for the different ways in which this reaction takes place[71].

Although the azide (IX) has found extensive applications, the mechanism of its reactions has not been established[72]. It may be that the intermediate (A) reacts intermolecularly with the amine or on dissociation gives rise to the acid azide (XVIII), which is converted into the amide (XV) as a result of bimolecular nucleophilic attack:



However, according to the authors of a review[5], the formation of the azide (VIII) has been insufficiently proved and the following mechanism can be considered for the formation of the amides (XV):

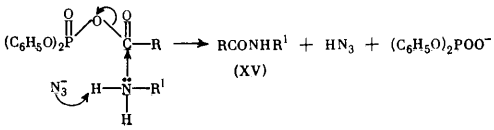
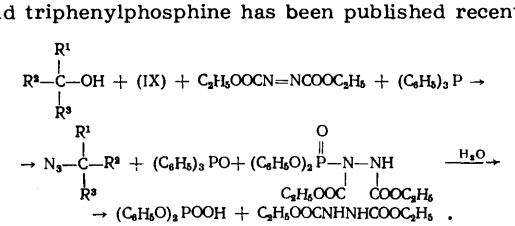


Table 9. The conversion of alcohols into azides using diphenyl phosphorazidate.

Alcohol	Azide	Yield, %
3β-Cholestanol	3α-Azidocholestane	78
Cholesterol	3α-Azido-5-cholestane	80—85
5α-Androsten-3β-ol-17-one	3α-Azido-5α-androsten-17-one	68
3α-Cholestanol	No reaction	—
5α-Androstan-17β-ol-3-one	No reaction	—
Cyclohexanol	Cyclohexyl azide	60
Decyl alcohol	Decyl azide	68
2-Menthol	(+)-Menthyl azide	90

The azide (IX) was used successfully to synthesise peptides in a high yield and without racemisation[32,68,73]. For example, the reaction of *N*-benzoxycarbonyl-L-leucyl-L-leucine with the hydrochloride of the methyl ester of L-valyl-L-phenylalanine has been achieved with a yield of 87%.[32]

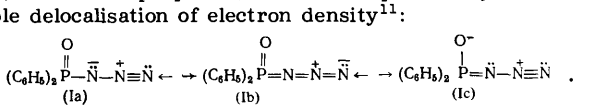
An elegant method of converting alcohols into azides by the reaction of the azide (IX), the diethyl ester of azodicarboxylic acid, and triphenylphosphine has been published recently[74]:



The reaction is stereospecific and makes it possible to obtain azides with high yields (Table 9).

3. Pyrolysis of PAA

The relatively high thermal stability of PAA, much higher than that of aryl and sulphonyl azides, has been noted. There is no satisfactory explanation of this phenomenon in the literature. The high thermal stability of diphenylphosphinic azide, for which different resonance structures (Ia–Ic) have been proposed, has been explained by the possible delocalisation of electron density[11]:



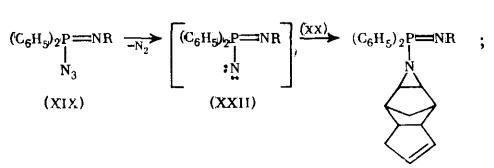
For thermally stable phosphorodiamidic azides, the possibility of a strong p_π–d_π conjugation between the α-nitrogen atom of the azide group and the phosphorus atom, has been noted[17].

Diphenyl phosphorazidate partly decomposes at 165 °C, darkens at 175 °C, and decomposes rapidly at 230 °C.[66] The extreme instability of the PAA in which there are several azide groups [triazidophosphine[4,25], phosphoric triazide[4,25], penta-azidophosphorane[25], and the azide $N_3P_3(N_3)_6$ [56]] should be noted.

Phenylphosphonic diazide and phenylphosphonothioic diazide decompose explosively above 80 °C,[14] while azidoperfluorodimethylphosphine explodes at 2–25 °C.[19] *N,N,N',N'*-Tetra-alkyl-*N''*-arylphosphorodiamidimidic azides decompose slowly at 150 °C with evolution of nitrogen[52]. For diphenylphosphinic azide, this temperature is above 137 °C.

Azidodiphenylphosphine decomposes at approximately 13.7 °C and is converted into the phosphonitrile $[(C_6H_5)_2PN]_x$. When attempts are made to vacuum distill (1 mmHg) diphenylphosphinothioic azide and diphenylphosphinoselenoic azide, they decompose[44]. All other PAA are stable on vacuum distillation and prolonged storage.

The evolution of nitrogen from the azide (XIX) has been noted only at 200 °C and in the presence of copper powder at 110 °C. In the presence of dicyclopentadiene (XX), a crystalline adduct (XXI) was obtained. It is formed when the nitrene (XXII) adds to dicyclopentadiene[75]:

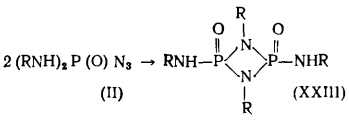


R = $SO_2C_6H_4CH_3$-*p*.

Various insertion reactions are characteristic of the nitrene formed on pyrolysis of sulphonyl azide[76]. It is known[77,78] that arenesulphonyl azides react with aromatic compounds at 105–120 °C to form *N*-aryl substituted arenesulphonamides. Under these conditions and also in the presence of azobisisobutyronitrile, diphenylphosphinic azide does not undergo this type of reaction[11]. Nor does it enter into the reaction with pyridine characteristic of sulphonyl azides[78,79]. The reduced reactivity of the azide group at the phosphorus atom has also been manifested by the fact that the azide (I) does not undergo a reaction of the type of the Schmidt rearrangement on treatment with boron trifluoride in ethereal solution (refluxing for 48 h).[11]

The above insertion reactions could not be carried out for phosphorodiamidic azides either[36]. Prolonged heating of the azides (II) *in vacuo* or in the presence of inert solvents at 150–200 °C leads to the formation of the imido-amides

RNHP(O)=NR, which have been isolated in the form of the dimers (XXIII):[5,36]



(II) (XXIII)

On pyrolysis (1 h, 380 °C) of diphenylphosphinic azide, the phenyl group is seen to migrate from the phosphorus atom to the nitrogen atoms[80] (aniline was detected among the hydrolysis products), but the structure of the reaction product was not investigated in detail[3].

4. Photolysis of PAA

The aim of studies on the photolysis of PAA was the detection of nitrene, the investigation of its reactions involving insertion into a C–H bond, and its capacity for rearrangements.

The photolysis of diethyl phosphorazidate, diphenyl phosphorazidate, and *N,N,N',N'*-tetramethylphosphorodiamidic azide (XXIV)[81] was investigated [the resistance of the azide (XXIV) to ultraviolet irradiation in benzene had been noted previously[17]]. The photolysis of a 0.01 M solution of diethyl phosphorazidate in cyclohexane yielded diethyl *N*-cyclohexylphosphoramidate (yield 88%) and ethyl phosphoramidate (12%). Both products are formed as a result of the attack of diethylphosphorylnitrene on the solvent. No products indicating a rearrangement of the nitrene were detected.

The results of the photolysis of phenyl azidoformate in cyclohexane are presented as a comparison—the yield of *N*-cyclohexylurethane, formed as a result of the insertion of the nitrene in a solvent molecule, was only 19%. The study of the products of the photolysis of the azides (IX) and (X) in 2-methylbutane showed that phosphorylnitrenes do not exhibit a very pronounced selectivity with respect to insertion in a C–H bond of the kind observed for nitrenes formed from $C_2H_5OC(O)N_3$, $t\text{-}C_4H_9C(O)N_3$, and $C_6H_5N_3$ (the products of insertion in a C–H bond involving a tertiary cation atom are formed preferentially in the last case)[81]:

$$(RO)_2P(O)\ddot{N} + (CH_3)_2CHCH_2CH_3 \rightarrow (RO)_2P(O)NHR^1;\ R=C_2H_5,\ C_6H_5;$$

(a) $R^1=CH_2CH(CH_3)CH_2CH_3$, (b) $R^1=(CH_3)_2CHCH_2CH_2$; (c) $R^1=(CH_3)_2CHCH(CH_3)$

(d) $R^1=CH_3CH_2C(CH_3)_2$.

For example, in the case of the azide (X) the product ratios are (XXVd):(XXVc):[(XXVa) + (XXVb)] = 6.0:4.3:1.0.

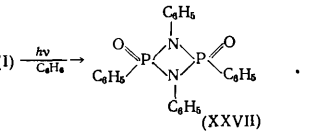
The high reactivity and low selectivity of phosphorylnitrenes were also observed on irradiation of a solution of the azide (X) in t-butyl alcohol[81]. Whereas the photolysis of ethyl azidoformate in t-butyl alcohol gives rise only to the product of the insertion in the O–H bond on photolysis, the product of the insertion in the C–H bond, namely the amide (XXVI), was also detected in the photolysis of the azide (X):

$$(C_2H_5O)_2P(O)\ddot{N} + (CH_3)_3COH \rightarrow \underset{(XXVI)\ (35\%)}{(C_2H_5O)_2P(O)NHCH_2C(CH_3)_2OH} +$$

$$[+\ \underset{(33\%)}{(C_2H_5O)_2P(O)NHOC(CH_3)_3} + \underset{(27\%)}{(C_2H_5O)_2P(O)NH_2}\ .$$

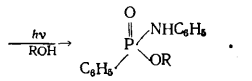
The phenyl[65], alkyl[48], and dimethylamide groups [in the photolysis of the azide (XXIV)][81] were found to migrate in phosphorylnitrenes from the phosphorus to the nitrogen atom, i.e. the photolysis of PAA is found to entail a rearrangement similar to the Curtius rearrangement. Derivatives of metaphosphonimidates# and an imidometaphosphate with the $O{=}\overset{|}{P}{=}N-$ fragment, which can dimerise or react with substances having a mobile hydrogen atom, are formed as intermediates.

Thus diphenylphosphinic azide gives rise to the diazadiphosphatidine (XXVII) on irradiation for 12 h (at 253.7 Å) in benzene:



(XXVII)

If the irradiation of the azide (I) is carried out in the presence of alcohols, then alkyl phenylphosphonanilidates are obtained[65]:



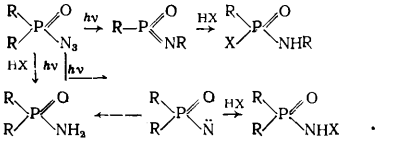
In other media the products of the addition of ethylene glycol, aniline, and methyl iodide to the metaphosphonimidate were obtained.

The photolysis of PAA has been studied in greatest detail in relation to di-t-butylphosphinic azide, di-isopropylphosphinic azide, and diethylphosphinic azide in various alcohols and in t-butylamine[48]. The results of the investigation are compiled in Table 10.

Table 10. Photolysis of dialkylphosphinic azides $R_3P(O)N_3$ in protic solvents[48].

№	Azide	Solvent (HX)	Yield, %		Other products
			$RP(O)(X)NHR$	$R_2P(O)NH_2$	
1	$(t\text{-}C_4H_9)_2P(O)N_3$	CH_3OH	71	—	$(t\text{-}C_4H_9)_2P(O)NHOCH_3$ (8%)
2	$(t\text{-}C_4H_9)_2P(O)N_3$	C_2H_5OH	62	24	none
3	$(t\text{-}C_4H_9)_2P(O)N_3$	iso-C_3H_7OH	27	64	none
4	$(t\text{-}C_4H_9)_2P(O)N_3$	$t\text{-}C_4H_9OH$	63	6.5	$(t\text{-}C_4H_9)_2P(O)NHCO_4H_9\text{-}t$
5	$(t\text{-}C_4H_9)_2P(O)N_3$	$t\text{-}C_4H_9NH_2$	74	—	none
6	$(iso\text{-}C_3H_7)_2P(O)N_3$	CH_3OH	71	5	$(iso\text{-}C_3H_7)_2P(O)NHOCH_3$
7	$(iso\text{-}C_3H_7)_2P(O)N_3$	C_2H_5OH	38	46	none
8	$(iso\text{-}C_3H_7)_2P(O)N_3$	$(t\text{-}C_3H_7OH$	—	87	none
9	$(iso\text{-}C_3H_7)_2P(O)N_3$	$(iso\text{-}C_4H_9NH_2$	74	—	none

The reactions can be illustrated schematically as follows:

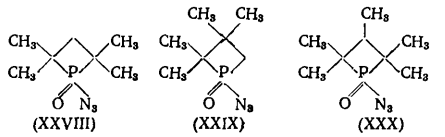


The addition of alcohols or t-butylamine to metaphosphonimidates results in the formation of alkyl *N*-alkylphosphonamidates or alkyl *N*-alkyl-*N'*-t-butylphosphonodiamidates. On passing from methanol to ethanol, the formation of dialkylphosphinic amides $R_2P(O)NH_2$ (compounds 2 and 7, Table 10) is observed, their yields increasing when the reaction is carried out in isopropyl alcohol (compounds 3 and 8), which can be accounted for by the ease of abstraction of hydrogen

#An analogy has been noted between the metaphosphonimidates and the isocyanates formed in the Curtius rearrangement of acyl azides[48].

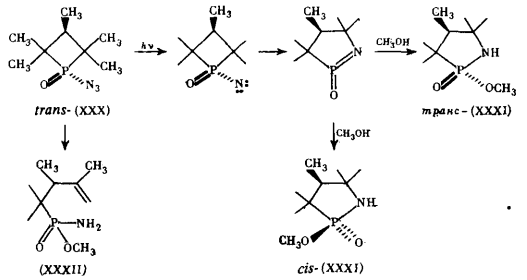
from the latter alcohol; the rate of the decomposition of the azide is several times greater than in methanol.

The migration of the alkyl group from phosphorus to nitrogen has also been observed in the nitrenes formed on photolysis of 1-azido-2,2,4,4-tetramethylphosphetan 1-oxide (XXVIII),[49] 1-azido-2,2,3,3-tetramethylphosphetan 1-oxide (XXIX),[49,82] and 1-azido-2,2,3,4,4-pentamethylphosphetan 1-oxide (XXX),[49,82,83] in methanol:



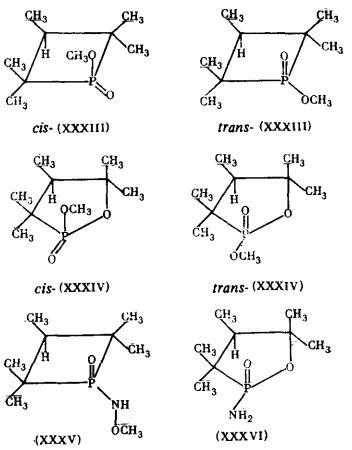
(XXVIII) (XXIX) (XXX)

The *trans*- and *cis*-isomers of compound (XXXI) and also compound (XXXII) have been obtained from the *trans*-isomer of compound (XXX):[49,82]



trans-(XXX) *транс*-(XXXI) (XXXII) *cis*-(XXXI)

The formation of the *cis*- and *trans*-isomers of compounds (XXXI), (XXXIII), (XXXIV), (XXXV), and (XXXVI) was demonstrated in a more detailed study[83] of the products of the photolysis of the *trans*-phosphetan (XXX):



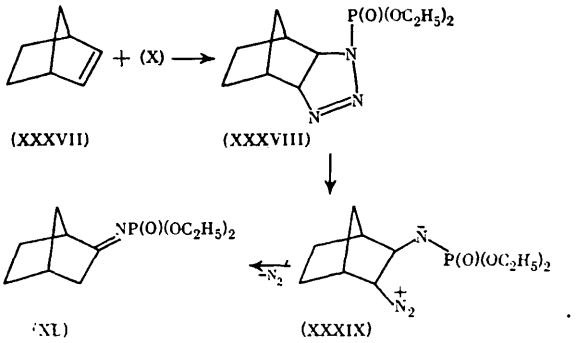
cis-(XXXIII) *trans*-(XXXIII) *cis*-(XXXIV) *trans*-(XXXIV) (XXXV) (XXXVI)

5. Reactions of PAA with Unsaturated Compounds (1,3-Dipolar Cycloaddition)

It has been shown in a number of studies[9,10,84-89] that PAA add to unsaturated compounds analogously to aryl azides and the azides of carboxylic acids.

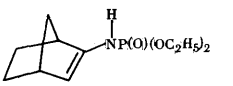
In relation to the addition of diethyl phosphorazidate to norbornene (XXXVII),[89] it has been suggested that the reaction proceeds via an intermediate triazoline (XXXVII), which is formed as the result of the 1,3-dipolar cycloaddition and is subsequently converted into the dipolar ion (XXXIX),

which decomposes with formation of *N*-(2-norbornylidene)-phosphoramidate (XL):



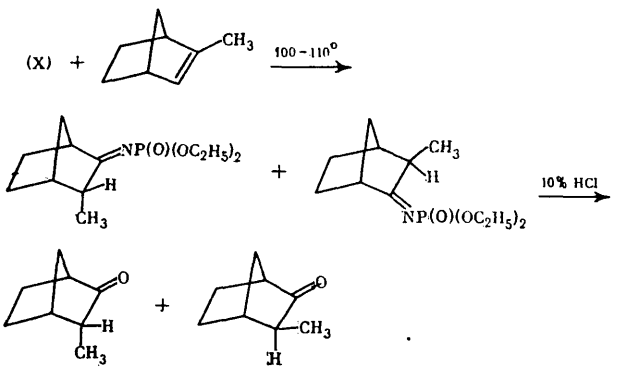
(XXXVII) (XXXVIII) (XL) (XXXIX)

A small amount (<5%) of the phosphoramidate

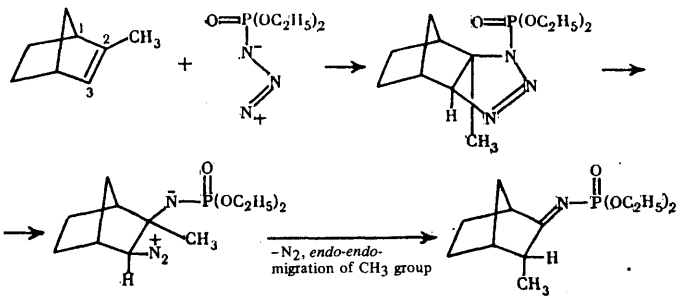


is also formed. The study of the reaction of norbornene deuterated in the 5- and 6-positions with the azide (X) led to the conclusion that the norbornyl skeleton does not rearrange. Dimethyl phosphorazidate reacts with compound (XXXVII) like the azide (X).[85]

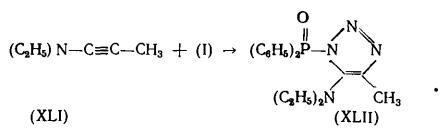
When the azide (X) adds to 2-methyl-2-norbornene, a mixture of diethyl *N*-(*endo*-3-methyl-2-norbornylidene)-phosphoramidate and diethyl *N*-(*exo*-2-methyl-3-norbornylidene)phosphoramidate is formed, but could not be resolved. However, after the hydrolysis of this mixture, *endo*-3-methyl-2-norbornanone (86%) and *exo*-3-methyl-2-norbornanone (14%) were isolated:



The intermediate triazolines were not isolated, since they are rapidly converted into phosphorylated imines as a result of the 3,2-*endo*-migration of the methyl group (the main reaction pathway) and the elimination of a nitrogen molecule[87]:

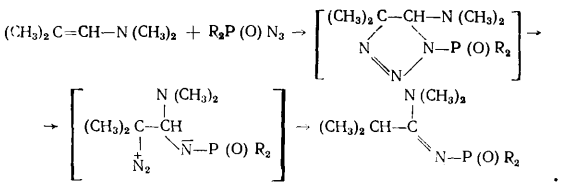


PAA react similarly with activated alkynes. Thus 1-(diethylamino)propyne (XLI) reacts with diphenylphosphinic azide in boiling benzene to form the triazole (XLII):[90]

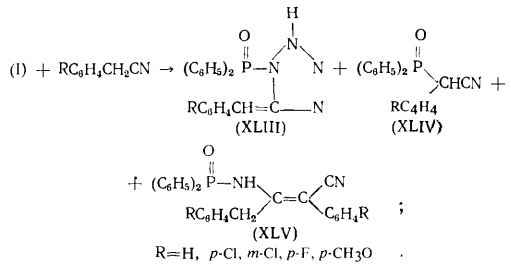


(XLI) (XLII)

The reactions of PAA with enamines give rise to high yields of phosphorylated amidines[9]:



The interaction of the azide (I) with substituted phenylacetonitriles led to the synthesis of the phosphorylated tetrazoline (XLIII), the nitrole (XLIV), and the enaminonitrile (XLV):[86]

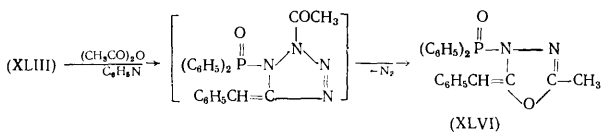


(XLIII) (XLIV)

(XLV)

R=H, *p*-Cl, *m*-Cl, *p*-F, *p*-CH_3O

The acylation of compound (XLIII) and subsequent heating yielded the phosphorylated oxadiazoline (XLVI):



(XLVI)

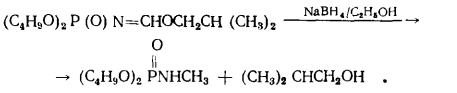
The reaction of PAA with vinyl ethers led to the formation of *N*-phosphorylated imines (XLVII) and phosphorylated triazolines, which were not expected[10]:

$$R_2P(O)N_3 + CH_2{=}CHOR^1 \rightarrow R_2P(O)N{=}CH{-}OR^1 + CH_2N_2 \qquad \text{(XLVII)}.$$

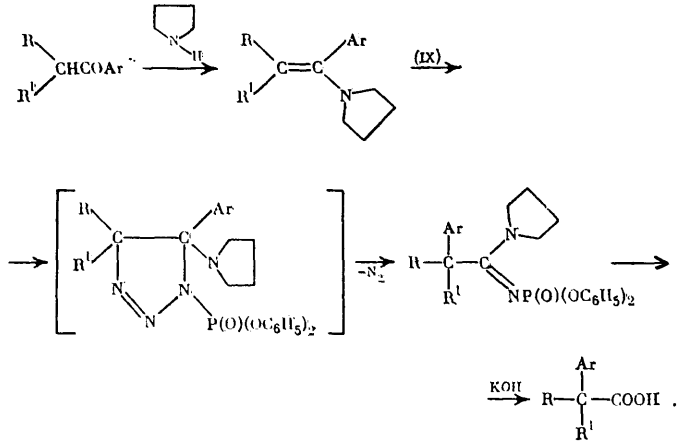
Hydrolysis of compound (XLVII) under mild conditions leads to the formation of *N*-formylphosphoramidates (XLVIII) and alcohols:

$$\text{(XLVII)} + H_2O \rightarrow R_2P(O)NH{-}CHO + R^1OH \qquad \text{(XLVIII)}.$$

The structure of compounds (XLVII) was confirmed in a study of the reaction with sodium tetrahydroborate, which involves the dissociation of the C–O bond:

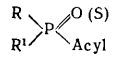


A method has been proposed for the conversion of alkyl aryl ketones into α-arylalkanecarboxylic acids using pyrrolidine and diphenyl phosphorazidate[91]. These reactions can be illustrated by the following scheme, in which the addition of the azide (IX) to the C=C double bond is postulated:



IV. PHYSIOLOGICAL ACTIVITY

Since the azide group in PAA has the properties of a pseudohalogen, the PAA fully satisfy the formula proposed by Schrader[92] for insecticides:



Indeed the first PAA [1,2] were patented as insecticides (dialkyl phosphorazidothioates—contact insecticides[1,93,94]; *N,N,N',N'*-tetramethylphosphorodiamidic azide—an effective systemic insecticide used against aphids).

Certain PAA exhibit a considerable toxicity for warm blooded animals. A strong miotic activity of diethyl phosphorazidate has been noted[8,30]. At the same time appropriate precautions made it possible to carry out an extensive research into this compound.

The toxicity and the anticholinesterase activity of certain phosphonamidic azides—derivatives of methylphosphonic acid have been investigated (Table 11).[42] The toxicity depends significantly on the structure of the amide component of the molecule—it has a maximum for the anilide group at the phosphorus atom.

Table 11. The toxicity and anticholinesterase activity of *N*-phenyl-*N*-alkoxycarbonyl-, and arylcarbamoyl-methylphosphonamidic azides[42].

Compound	Toxicity, mg kg^{-1}		I^*_{50}, moles
	LD_{50}	LD_{100}	
$CH_3P(O)(N_3)NHC_6H_5$	2.692	5	$4.5\cdot10^{-7}$
$CH_3P(O)(N_3)NHCOOCH_3$	1.39	5	$3.0\cdot10^{-6}$
$CH_3P(O)(N_3)NHCOOC_2H_5$	83.18	100	$8.0\cdot10^{-5}$
$CH_3P(O)(N_3)NHCOOC_3H_7$-iso	20.89	25	$4.0\cdot10^{-6}$
$CH_3P(O)(N_3)NHCONHC_6H_5$	851.1	1000	$1.0\cdot10^{-2}$
$CH_3P(O)(N_3)NHCONHC_6H_4Cl$-*p*	952.0	1000	$1.0\cdot10^{-2}$

*I_{50} represents the molar concentrations of the inhibitor which cause a 50% suppression of enzyme activity in 5 min.

The following series based on the dependence of the toxicity on the structure of the alkoxy-group has been observed for alkoxycarbonylamido-substituted PAA: methoxy > isopropoxy > ethoxy. Amido-substituted derivatives of ureidoazidomethylphosphonic acid exhibit a minimal toxicity.

V. PHYSICAL PROPERTIES

1. Infrared and Raman Spectra

PAA are characterised by an intense absorption band corresponding to the antisymmetric N–N stretching vibrations in the N_3 group. The band, which occurs at 2138–2195 cm^{-1} (3,25, 44–46) has a higher frequency than for organic azides (in the vicinity of 2130 cm^{-1})[95]. As for organic azides, the corresponding symmetrical vibrations have a much lower frequency and their absorption bands are much less intense.

Various types of vibrations characteristic of PAA have been examined in detail in a dissertation[45]. Some of them, localised either in the group of nitrogen atoms or in the group of phosphorus and nitrogen atoms, will be presented here.

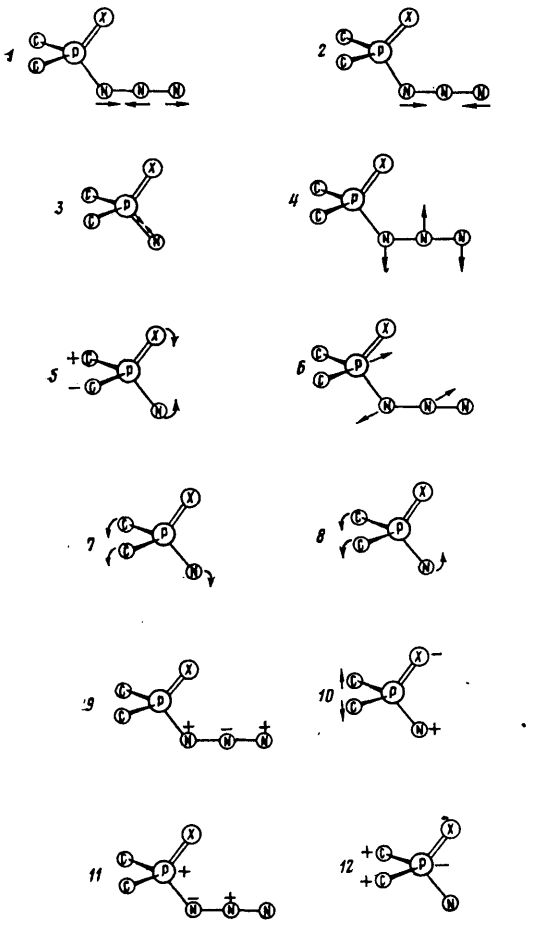


Figure 1. The types of vibrations of the $C_2P(X)N_2$ (X = O, S, or Se) fragment characteristic of PAA;[45] 1) $\nu_{as}(N_3)$; 2) $\nu_s(N_3)$; 3) ν(P–N); 4) $\delta(N_3)$; 5) $\delta[C_2P(X)N]$; 6) δ(P–N–N); 7) $\delta(C_2PN)$; 8) $\rho(C_2PN)$; 9) $\gamma(N_3)$; 10) $\tau[C_2P(X)N]$; 11) γ(P–N–N); 12) $\omega[C_2P(X)N]$.

The first group (Fig.1, *1–8*) includes stretching and deformation vibrations symmetrical relative to the plane. They must be active both in the infrared absorption and Raman spectra; in the latter case they should give rise to polarised lines.

In the second group (Fig.1, *9–12*) the stretching and deformation vibrations are antisymmetric relative to the plane; they are also active in the infrared absorption spectra, while in the Raman spectra depolarised lines correspond to them.

Table 12 presents the infrared and Raman spectroscopic data for dimethylphosphinic azide[44]. The insignificant ν_{as} intensity in the Raman spectrum is noteworthy (Fig.2). The antisymmetric vibration characteristic of PAA can be used for analytical purposes. When PAA were allowed to react with phosphorus(III) compounds, the end of the reaction was inferred from the disappearance of the azide band in the infrared spectrum of the reaction mixture[31].

Table 12. The wavenumbers (ν, cm^{-1}) in the vibrational spectra of dimethylphosphinic azide[44].

i.r.	Raman	Assignment	i.r.	Raman	Assignment
3397 w.	—	$\nu_{as} + \nu_s(N_3)$	554 v.s.	552 v.s.	ν (P—N) + $\delta(N_3)$
2521 w.	—	$2 \times \nu_s(N_3)$	393 s.	399 m.	$\delta[C_2P(O)N]$
2143 v.s.	2150 m.	$\nu_{as}(N_3)$	317 v.w.	312 m.	$\omega(PC_2N)$
1268 v.s.	1269 m.	$\nu_s(N_3)$	260 m.	258 s.	$\rho[C_2P(O)N]$
735 s.	732 w.	ν (P—N)+ $\delta(N_3)$	—	142 s.	$\tau[C_2P(O)N]$

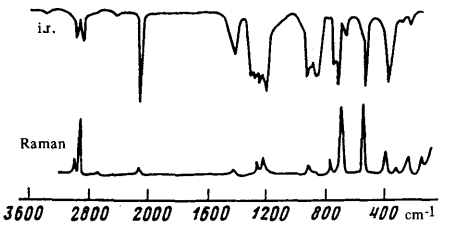
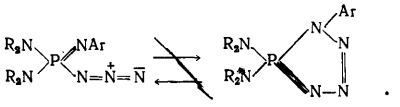


Figure 2. Infrared and Raman spectra of dimethylphosphinic azide[44].

The study of the infrared spectra of PAA confirmed their structure. The relative intensity of the azide absorption band at 2140 cm^{-1} in the spectra of *N,N,N',N'*-tetra-alkyl-*N''*-arylphosphorodiamidimidic azides is independent of the solvent (CCl_4, dioxan, and pyridine). This disproves the possibility of the azido-tetrazole tautomerism[52]:



A similar tautomerism has been ruled out for phosphinimidic acid azides $[(C_6H_5)_2P(=NR)N_3]$ [22,96,97] and diethyl phosphorazidate[8].

2. NMR Spectra and Mass Spectra

The chemical shifts of the signals in the ^1H, ^{13}C, and ^{31}P NMR spectra of PAA and the corresponding chlorides have been compared[28,44–46]. The ^{14}N NMR data for certain PAA and ^{15}N NMR data for isotope-substituted PAA have been published[98].

Mass-spectrometric data for PAA have also been published[44-46]. In the mass spectra of dimethylphosphinic azide $(CH_3)_2P(O)N_3$ and its deuterated analogue $(CD_3)_2P(O)N_3$, the fundamental peaks 77 $[(CH_3)_2PO^+]$ and 83 $[(CD_3)_2PO^+]$ correspond to the loss of the entire nitrogen $(M^+ - 42)$.[45] It is noteworthy that the fundamental peak in the mass spectrum of phenyl azide corresponds to the loss of molecular nitrogen $(M^+ - 28)$.[99]

3. The Atomic Refraction of the N_3 Group

The atomic refraction of the N_3 group in PAA has come to be assumed to be 9.61 cm^3 (calculated from the results of Gilyarov and coworkers[23,31]; the Eisenlohr numbers have been used for the atomic refractions of other elements), i.e. it is close to the atomic refraction of the N_3 group in alkyl and aryl azides[100].

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The advances in PAA chemistry are evident. Like any vigorously developing field of study, the chemistry of PAA involves many unsolved problems, some of which have been formulated in this review. It has now become necessary to manufacture in the USSR diphenyl phosphorazidate, the employment of which in the "modified Curtius reaction" instead of nitrous acid will undoubtedly prove useful in organic synthesis.

It may be hoped that this review will stimulate interest in the chemistry of PAA and this will assist in its further development.

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Advances in the Chemistry of Phosphorus(III) 1,3,2-Diheterophosphorinanes

E.E.Nifant'ev and A.I.Zavalishina

Studies on the synthesis and chemical reactions of 1,3,2-diheterophosphorinanes containing a tervalent phosphorus atom are examined for the first time within a single review. The influence of the heteroatoms surrounding the phosphorus atom on the properties of the phosphorinane system is analysed. The chemical features of mono- and poly-cyclic 1,3,2-diheterophosphorinane are compared and the ways of the practical utilisation of these substances are discussed.
The bibliography includes 338 references.

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I. INTRODUCTION

Phosphorus(III) 1,3,2-diheterophosphorinanes (DHP) constitute a large group of six-membered heterocycles whose molecules contain a tervalent phosphorus atom surrounded by other heteroatoms. Here one should include also the corresponding hydrophosphoryl, hydrothiophosphoryl, and hydroiminophosphoryl compounds, one of the tautomeric forms of which contains a tricoordinate phosphorus atom. The phosphorus–oxygen heterocycles, namely 1,3,2-dioxaphosphorinanes (DOP) have been investigated most thoroughly but in very recent years related systems have begun to be considered: diazaphosphorinanes (DAP), oxazaphosphorinanes (OAP), and dithiaphosphorinanes (DTP).

The first examples of DHP were synthesised in the Soviet Union[1] and in the United States[2] at the end of the 1940's. During this period, the reasons for the interest in these compounds were largely classified and the volume of work was therefore small. It was not until the 1970's that the chemistry of the DHP was sharply activated, in connection with the development of much interest during this period in the comparison of the stereochemistry and reactivity of cyclohexanes and saturated heterocycles. In addition, at this time realistic methods became available for the investigation of the electronic structure of the DHP and particularly the elucidation of the nature of the interaction of the electron pairs and orbitals of the triad $-\ddot{X}-P-\ddot{Y}-$, which is incorporated in six-membered rings with different degrees of rigidity. Finally, the development of the chemistry of DHP was stimulated by the publication of novel synthetic studies, including those leading to the solution of important applied problems. Ultimately the interests of specialists in organophosphorus synthesis, stereochemistry, spectroscopy, complex catalysis, bio-organic chemistry, and the chemistry of high-molecular-weight compounds coincided in the study of the DHP. Because of this, an extensive scientific field was established, the

principal achievements in which are discussed in the present review.

The chemical behaviour of DHP is mainly determined by two factors: the nature of the central functional group and the overall structure of the molecule. In dealing with the structure of the molecule, one must bear in mind whether the substance belongs to mono- or poly-cyclic systems, since the latter frequently have chemical properties which are not altogether usual. In this connection, we subdivided the entire contents of the review into two parts, devoted to the mono- and poly-cyclic systems.

In each section the synthesis and partly the stereochemistry are considered initially and then the chemical properties of the DHP.

Since the appendix to the Russian translation of the book of Purdela and Vilceanu[3] gives a list of publications on phosphorus-containing heterocycles covering the literature up to 1969, in the present review attention has been concentrated only on studies of the latest period.

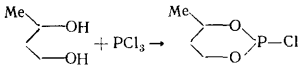
II. MONOCYCLIC 1,3,2-DIHETEROPHOSPHORINANES

1. Synthesis

DHP can be obtained using two approaches. The first combines the phosphocyclisation of 1,3-glycols and similar 1,3-bifunctional compounds, i.e. reactions leading to the formation of six-membered phosphorus-containing heterocycles from linear systems. Data on this problem are discussed in this section separately for DOP, DAP, and DTP. The system adopted is dictated by the non-uniformity of the studies on different DHP and also by the fact that they are not always produced by general methods. The second approach is based on the exchange reactions of the substituents at the phosphorus atom already incorporated in the phosphorinane ring. The corresponding data are considered in the next section which deals with the chemical reactions of DHP. This procedure eliminates the possibility of repetitions and makes it possible to relate the problem of the synthesis of individual classes of DHP to their general chemical characteristics.

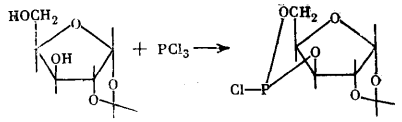
(a) 1,3,2-Dioxaphosphorinanes

When 1,3-diols react with phosphorylating agents having at least two leaving groups, it is possible to obtain different types of DOP. Phosphorus trichloride has been used as the phosphorylating agent in many investigations[1,2,4-8], for example:

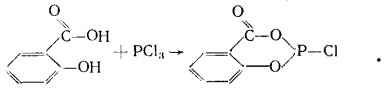


The reaction is usually carried out in a dry solvent. A tertiary amine is not always used to combine with the hydrogen chloride evolved. The hydrogen chloride is then removed from the reaction mixture by bubbling in a dry inert gas. This feature, apparently associated with the anomalously low basicity of cyclic phosphorochloridites, greatly simplifies the synthesis of chlorophosphorinanes and distinguishes it from the synthesis of dialkyl phosphorochloridites.

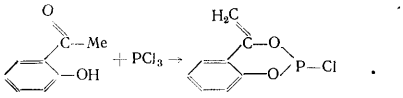
The condensation of phosphorus chloride has been widely investigated. A wide variety of halogenated glycols[9], the corresponding unsaturated systems[10], ethers[6,11,12], and nitro-compounds[13] have been made to undergo this condensation. In this case the possibility of a partial oxidation-reduction reaction, leading to nitrosoglycols and phosphoryl compounds, has been noted[13]. In addition, the cyclophosphorylation of the polyfunctional system of the antibiotic synthomycin[14] and 1,2-isopropylidenexylofuranose[15] has been achieved:



We shall consider the stereochemical aspect of the phosphorylation with phosphorus trichloride. A single stereoisomer, whose chlorine atom occupies an axial position, is as a rule formed in this case[15-20]. The reaction of phosphorus trichloride with 2-benzylglycerol, leading to a mixture of unequal amounts of two stereoisomers, is an exception[12]. Salicylic acid reacts with phosphorus trichloride similarly to β-glycols[21]:

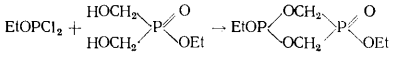


As regards the chemical aspect, the analogous phosphorylation of acetylacetone and 2-acetylphenol, leading to unsaturated DOP, is of great interest[22]:



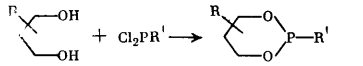
Unfortunately this synthesis has not yet been widely developed. Among other phosphorus trihalides, only phosphorus tribromide has been made to react with diols, 2-bromo-1,3,2-dioxaphosphorinane being obtained[18,23].

Numerous studies have been devoted to the cyclophosphorylation of 1,3-diols with tervalent phosphorus acid dichloride. In particular, a detailed study has been made of the interaction of glycols with Menshutkin acid chlorides in the presence of bases[6,7,15,24,25]. The cyclisation reaction[26]



is promising in many respects.

The dichloride of phosphorus acids react with 1,3-glycols similarly to the Menshutkin acid chlorides. This makes it possible to obtain interesting cyclic phosphonites albeit not always in high yields[24,27-30]:

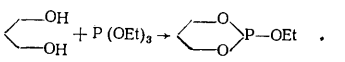


We may also note that the condensation reactions with phosphonous acid dichlorides are of less universal importance than the corresponding reactions with phosphorus trichloride owing to the occurrence of side reactions[31].

In its stereochemical aspect, the phosphocyclisation with acid dichlorides differs from the cyclisation with phosphorus trichloride. When asymmetric glycols are used, not one but two interconvertible stereoisomers are formed, in which the axial position is preferred for the alkoxy-group.

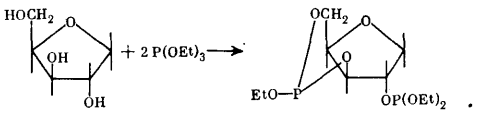
The reactions discussed above have attracted attention because of the outward simplicity of their mechanism and the availability of phosphorylating agents. Nevertheless, they do not always yield good results owing to the presence of hydrogen chloride, which is not completely bound by the acceptors employed. A significant factor for larger-scale syntheses is also the fact that many reactions involving

phosphorus chloride require the employment of large volumes of dry solvents. Bearing this in mind, alternative cyclophosphorylation methods have begun to be studied in many laboratories, including those dealing with applied problems. The transesterification method was the first to be studied in detail, for example:



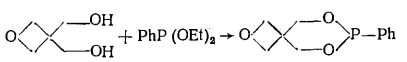
It has been shown that various forms of glycols[4,9,18,33,34] readily interact with the simplest neutral phosphorus acid esters. It has been suggested that this reaction be used to simplify industrial polymer stabilisers[32].

The reaction of xylitan, which is an asymmetric triol, with an excess of triethyl phosphite merits special attention. The β-glycol group in xylitan ensures the selective formation of the phosphorinane ring; the second of the *trans*-vicinal hydroxyls is more passive and is phosphorylated without cyclisation:



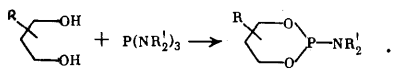
A similar regioselectivity has also been noted in the phosphorylation of 2,4-methylenexylitan[35].

Neutral phosphonites can also be transesterified with 1,3-glycols,[36,37] including those with other functional groups. As an illustration, we may quote the synthesis of the spirocyclo system[36]



Dialkyl phosphites are also involved in transesterification with various β-glycols. This results in the formation of DOP belonging to the class of hydrophosphoryl compounds[4,12,38-42]. A mixture of two geometrical isomers of DOP is usually obtained as the technical product. One of them, which has the phosphoryl group in the equatorial position, crystallises out[38-40,43].

In the latest studies the phosphorylation of 1,3-diols is usually carried out using the triamides of phosphorus acid[34,38,39,42,44-47]:



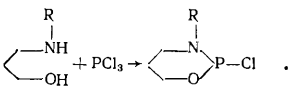
The reaction is carried out simply and under mild conditions in the absence of corrosive side products and is very productive. Because of this, it has found extensive preparative applications, particularly in a series of complex systems. Thus it has been used in the synthesis of aminophosphorinanomonoses[15,25,40] and nucleosides[47,48].

The problem of the configuration of the phosphorus centre in 2-amino-DOP has been discussed in the literature. From NMR data, it has been concluded that the position of the amino-group depends on the nature of the substituents at the nitrogen atoms[45,49-52]. The unusual equatorial disposition is probably promoted by the orbital interaction of the nitrogen and phosphorus; on the other hand, if the unshared electron pair of the nitrogen atom is delocalised over the structural elements of the amino-group, then the axial disposition of the substituent obtains more readily[52].

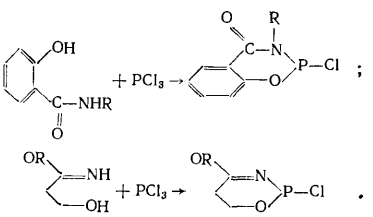
The diamides of alkylphosphorus[48,53], arylphosphorus[53], and phosphonous[54] acids are also effective phosphorylating agents. Many DOP, particularly those derived from sterically hindered phenols[53], sugars[25], and nucleosides[48], have been obtained on their basis.

(b) 1,3,2-Oxaphosphorinanes

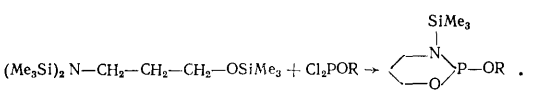
OAP have been vigorously investigated in the last ten years, mainly in connection with the requirements arising in the development of bio-organic chemistry. They are synthesised from β-aminoalcohols in different ways depending on the nature of the latter. *N*-Alkyl-[55-59] and *N*-aryl-propanolamines[55] react with phosphorus trichloride in the presence of triethylamine to form 2-chloro-oxazaphosphorinanes:



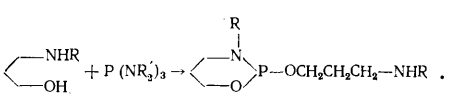
The amides of salicylic acid[60] and the iminoesters of β-hydroxypropionic acid[61] have been similarly condensed with phosphorus trichloride to form OAP with functional groups:



The phosphocyclisation is also carried out using the dichlorides of alkylphosphorous[57,60,62], phosphoramidous[57,63], and phosphonous[64] acids. The dichlorides of alkylphosphorous acid are condensed with *O,N,N*-tri(methylsilyl)propanolamine[65]:

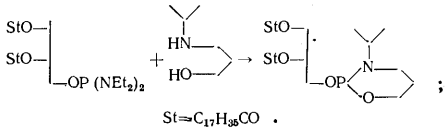


The most frequently employed method of synthesis of OAP involves the interaction of 1,3-aminoalcohols or their derivatives with a tervalent phosphorus acid amides, unexpected results being obtained. The simplest instance of such cyclisation is the interaction of secondary aminoalcohols with the triamides of phosphorous acid. It has been stated in a patent[55] that, for an equimolecular reactant ratio, 2-amino-OAP are obtained. However, it was shown later[57] that, for different ratios of reactants, different substances are formed, namely 2-γ-aminopropyl-OAP:



A similar type of phosphocyclisation has also been described for the phosphorylation of unsubstituted propanolamine with phosphorus acid triamides[66]. This result, i.e. double phosphorylation, is apparently associated with the higher reactivities of 2-amino-OAP, which are intermediates in this synthesis, than those of phosphorus acid triamides. Triamides of phosphorous acid readily phosphorylate *N*-acetylpropanolamine[67,68]. The absence of secondary phosphorylation is entirely logical, because the basicity of the phosphorus atom (the most important factor in reactivity) in 3-acetyl-2-amino-OAP is significantly reduced.

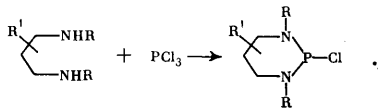
Phosphorodiamidites react with an equimolar amount of propanolamine[62,69,70], *N*-alkylpropanolamine[57,71,72], and *N*-acylpropanolamine[68] to form OAP of different types, including those which belong to the class of phospholipids as regards their structure, for example[72]:



St=$C_{17}H_{35}CO$.

(c) 1, 3, 2-Diazaphosphorinanes

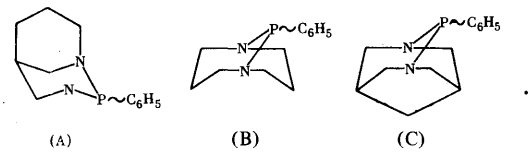
DAP began to be studied later than OAP but more extensively. Initially they were synthesised successfully by the reactions of secondary 1,3-diamines with tervalent phosphorus acid halides. Numerous studies have been devoted to phosphorylation with phosphorus dichlorides[73–78]:



A wide variety of chlorides of 1,3-alkylenephosphorodiamidic acid chlorides, which exist in the form of a single isomer in which the chlorine atom has the axial orientation, have been synthesised by the above methods[73,76,79]. 2-Chloro-4-methyl-1,3-diphenyl-DAP, which consists of two isomers, is an exception. Bearing in mind the results of Belov et al.[80], one may postulate that the chlorine atom in the systems considered occupies the axial position.

Experiments with secondary amides of β-alkylaminopropionic[81] and *N*-alkylanthranilic[82,83] acids have been described, but pure 2-chloro-4-oxo-DAP were not obtained. Nevertheless the technical products have been used successfully in further extremely complex reactions[83].

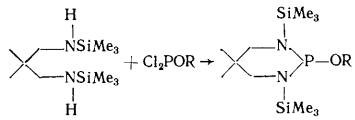
The dichlorides of alkylphosphorous[73,78], phosphoroamidous[73,76,78]†, and phosphonous[73,76] acids usually react with secondary 1,3-diamines to form various DAP. Together with linear diamines, their cyclic analogues began to be studied in the phosphorylation reaction, which makes it possible to synthesise "bulky" DAP of great stereochemical interest[73], for example:



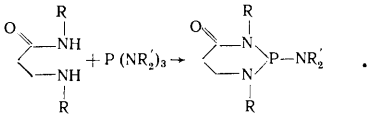
(A) (B) (C)

The chemical shifts of the phosphorus atom in these derivatives are determined by the geometry of the molecules to a significant extent : 94.3 p.p.m. for (A), 103.6 p.p.m. for (B), and 180.8 p.p.m. for (C).

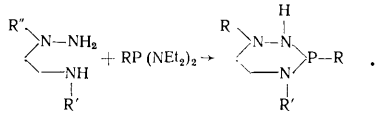
N-Silylated DAP are formed when Menshutkin acid chlorides react with bisdisilylated 1,3-diamines[84]:



The second method of synthesising the diazaphosphorinane ring is based on the transamidation of the amides of tervalent phosphorus acids. It is experimentally simple and is of great synthetic value. Thus the full amides of phosphorous acids phosphorylate extremely effectively secondary diamines[77] and aminoamides[81]:



We may note that the reaction of phosphorous acid triamides with secondary 1,3-diamines does not suffer from the limitation which we have considered for the reaction with propanolamines. This indicates some difference in the phosphorylation of related diamines and aminoalcohols and possibly amines and alcohols in general. The diamides of alkylphosphorous acid have been investigated in the reaction with primary 1,3-diamines, which made it possible to obtain the hitherto unavailable but very promising DAP without substituents at the nitrogen atoms[84]. The diamides of phosphonous acids have been made to react with aminohydrazines. Condensation resulted in the synthesis of the first representatives of 1,2,4,3-triazaphosphorinanes[85]:



It may be supposed that the proposed condensations will permit the synthesis in the immediate future of a large number of new DAP of interest for structural and synthetic research.

(d) 1, 3, 2-Dithiaphosphorinanes

This field of synthesis of DHP has been studied very much less than those already discussed, which reflects the overall picture showing that the thiol esters of tervalent phosphorus acids have been little investigated. Nevertheless, it has already been established that some of the simplest DTP are chemically very unusual; furthermore, they exhibit insecticidal and herbicidal activities[86].

1,3-Dithiols interact with phosphorus trichloride in the presence of tertiary amines to form 2-chloro-DTP.[86–88] The dichlorides of alkylphosphorous[89], alkylphosphorothious[88], phosphoroamidous[87], and phosphonous[88–93] acids, have also been used as phosphorylating agents. It has been noted[91] that DTP dimers are formed together with the DTP themselves. The problems of the stereochemistry of DTP have been examined in a number of studies[89,93–95]. Azathia- and oxathiaphosphorinanes have not so far been described in the literature.

2. Chemical Properties

In writing this section of the review, the authors had two aims: to carry out a subject survey of synthetic studies and to examine the characteristics of the chemical behaviour of DHP determined by their cyclic structure. The latter aim presupposes in its turn the analysis of the electronic structure and intramolecular dynamics of DHP, which is at present difficult to achieve in the required detail despite the progress made, for example, in the study of Arshinova[96]. However, it is possible to make introductory remarks which will draw the reader's attention to the problem and will help him to become acquainted with the factual data.

† The reaction has no general importance and is very unusual in its chemical aspect. Its analysis will be described in the section dealing with the chemical properties of DHP.

An ordered orientation of the unshared electron pairs of the heteroatoms, which is absent from the corresponding acyclic systems, is characteristic of DHP [97–99] and presumably the n_P–n_O interaction is blocked in DOP by virtue of such order. This is confirmed by a comparison of photoelectron spectroscopic data and the chemical properties of acyclic and cyclic compounds. The problem of the involvement of the electron pairs of the nitrogen atoms of OAP and DAP in the n_P–n_N interaction is more complex, since in this case their orientation can generally speaking depend on the influence of the substituents present.

The orientation of an exocyclic substituent at the phosphorus atom plays a significant role in the chemical characteristics of monocyclic DHP. If the substituent having n or π electrons is axial, its electrons are less effectively delocalised than those of a similar equatorial substituent. This difference is probably associated with the blocking of an interaction of the n_P–n_X type on the assumption of the axial position.

Another feature of the DHP consists in the somewhat small number of their conformational transitions[100]. The limited number of such transitions is thrown into particular relief when substituents are introduced into the hydrocarbon part of the ring or when an additional ring is condensed. Henceforth the possibility of synthesising in the series of DHP rigid systems in which the central and additional functional groups are located in space in such a way that they can ensure attack from unusual directions and hence also unusual types of reaction. Having outlined this situation, we formulated the principle of the stereochemical regulation of the reactivity in the series of cyclic derivatives of tervalent phosphorus acids. This principle has already been realised in the reactions of DHP.

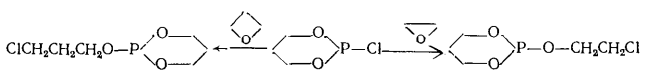
Since numerous scientific articles and patents have been devoted to the reactions of monocyclic DHP, the relevant data are discussed separately in terms of classes of compounds.

Within each section the data are further subdivided on the basis of the principal structural-chemical features. The following characteristics are discussed in succession for the usual DHP: (1) substitution reactions involving an exocyclic substituent at the phosphorus atom; (2) protonation and oxidation reactions; (3) Arbuzov alkylation and related syntheses; (4) other processes. After this, the chemical properties of DHP, which are prototropic systems (hydrophosphoryl and thiohydrophosphoryl substances), are discussed in separate subsections.

(a) 1, 3, 2-Dioxaphosphorinanes

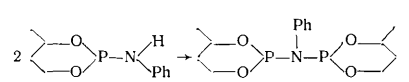
Substitution reactions at the phosphorus atom. The nucleophilic substitution of chlorine in 2-chloro-DOP has been studied in greatest detail. These compounds are readily converted into neutral phosphites in their reactions with alcohols[6,7,10,15,22,101–103], phenols[7,104,105], substituted glycerols[106,107], and sugars[15,107,108] in the presence of bases. The problems of the stereochemistry of the reaction and the characteristics of the steric organisation of the cyclic neutral phosphites obtained have been examined in a number of studies[101,102,107,109,110].

2-Chloro-DOP can be converted into the corresponding neutral phosphites even on treatment with oxirans and oxetans[111,112], for example:

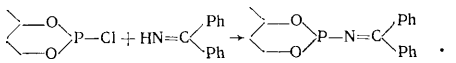


Six-membered cyclic phosphorochloridites react with mercaptans to form phosphorothioites (see, for example, Okruszek and Stec[113]).

Numerous communications contain data concerning the interaction of 2-chloro-DOP with nitrogen-containing bases of different types. Arbuzov and Zoroastrova showed for the first time[114] that 1,3-alkylene phosphorochloridites react with a simplest secondary amides to form 2-amino-DOP. Subsequently this reaction came to be widely employed[10,12,15,34,102,115,116]. It was shown that, when amines are phosphorylated by asymmetric cyclic chlorides, a mixture of two isomers is always formed[19,51,102,110]#. Primary amines in general behave in this reaction analogously to secondary amines[49,50,114,118], although they yield less satisfactory results on a preparative scale. This is associated with the disproportionation, first investigated in relation to the anilide of 1,3-butylenephosphorous acid[118]:

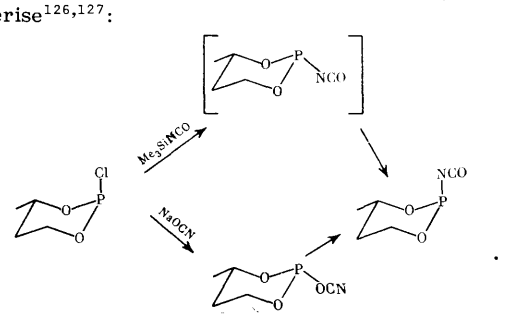


In the presence of bases, imines are also phosphorylated by 2-chloro-DOP in accordance with the general mechanism, for example[119]:



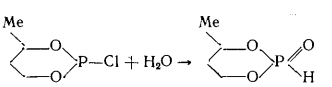
Instead of amines, it is possible to use their *N*-trimethylsilyl or magnesium derivatives.

2-Chloro-DOP exchange the chlorine atom for many groups on interaction with salts of acids or their trimethylsilyl derivatives. Thus the reaction with antimony trifluoride yields fluorides[8], that with carboxylic and alkylcarbonic acid salts gives rise to acylates[120,121], the reactions with cyanotrimethylsilane[122], silver cyanate[123], or hydrocyanic acid in the presence of triethylamine results in the formation of cyanides[124], and the reaction with isothiocyanatotrimethylsilane yields isothiocyanates[125]. The reaction with cyanic acid derivatives is of special interest. *N*-Trimethylsilyl derivatives leads to phosphoisocyanates, while salts of cyanic acid result in the initial formation of the *O*-isomers, which then isomerise[126,127]:



2-Chloro-DOP react with sodium dialkyl phosphites to form asymmetric pyrophosphites (*O*-phosphorylation of the ambident phosphite anion[128]), while their reaction with *N*-trimethylsilylacetamide gives rise to acid cyclic phosphites[129]. The latter reaction probably involves the *O*-phosphorylation of the silyl derivative with formation of the phosphiminoacetate, which then decomposes splitting off acetamide.

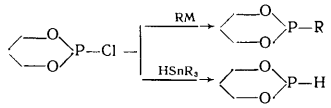
The hydrolysis of 2-chloro-DOP to cyclic hydrophosphoryl compounds has been studied in detail[7,10,12,15,33,117,130], for example:



This problem has been treated erroneously by Bodkin and Simpson[117].

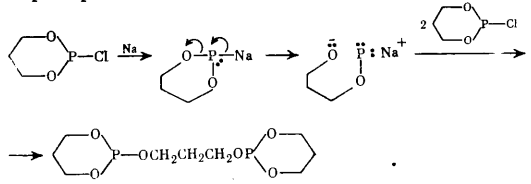
The hydrolysis of asymmetric phosphorochloridites results in the formation of two isomers, the stable isomer, with an equatorial phosphoryl group, crystallising out[43,117]. The sulphydrolysis of 2-chloro-DOP leads to cyclic hydrothiophosphoryl compounds[130,131]. The problems of the stereochemistry of this reaction have been studied[131].

The consideration of the substitution of chlorine in the series of DOP will be completed by examining reactions with organometallic compounds and metals. It has been suggested that the following reactions take place with Grignard and Norman reagents[132] and with tin hydrides[110,133]:



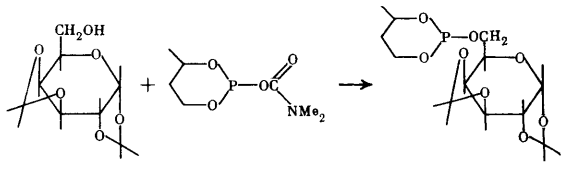
The cyclic esters of hypophosphorus acid obtained are of definite interest as the parent members of the series of DOP. Using them, it is possible to determine the stereochemistry of phosphorus in various DOP by comparative ^{1}H and ^{13}C NMR.[110]

The 2-chloro-DOP do not react with alkali metals in an altogether usual manner[134]§. The process probably begins with one-electron transfer and involves the stage in which P-metallated DOP are formed. The latter decomposes owing to the concerted donor–acceptor action of the geminal substituents at the phosphorus atom. The polar intermediate undergoes further reduction and phosphorylation with formation of diphosphites:



If 2-chloro-DOP is treated with other metallating and even silylating agents, for example, triphenyl-lithiosilane, then a diphosphite is also obtained[134].

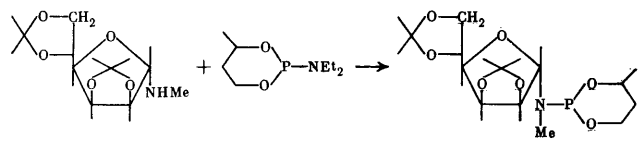
2-Acyloxy-DOP are similar to 2-chloro-DOP as regards reactivity. These compounds have found applications as phosphorylating agents and are used in the synthesis of certain cyclic phosphites[120,121]. Their advantage is that in the acylation of nucleophiles less corrosive carboxylic, alkylcarbonic, and carbamic acids are evolved instead of hydrochloric acid, as mentioned above. As an illustration of the foregoing, we may quote the following examples[136]:



The hydrolysis[128] and acidolysis[137] of the above cyclic acyl phosphites gives rise to hydrophosphoryl compounds. The same result has been noted in the decarboxylation of formyl phosphites[138].

Other popular reagents frequently used for the purposes of fine organophosphorus synthesis are the amides of 1,3-alkylenephosphorous acids. These compounds are readily available, convenient to work with, and exhibit the optimum reactivity in many reactions. When they are used in phosphorylation, the amine is evolved, but it does not as a rule complicate the process and is readily removed from the reaction mixture. 2-Amino-DOP readily phosphorylate alcohols[7,40,47,115,139–143], phenols[7,140,144], substituted glycerols[106,107], and sugars[15,107,108,145]. An important factor is the difference in the ease of interaction of the two geometrically isomeric amides with alcohols[139].

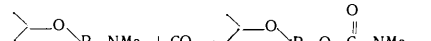
A series of studies has been devoted to the phosphorylation of amines by transamination[141,146]. Very recently transamination has been used to synthesise new systems—phosphoglycosylamines[147]:

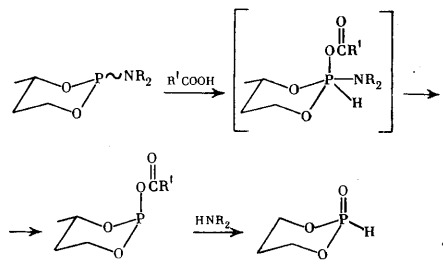


The interaction of 2-amino-DOP with carboxylic acids has been described in the literature. If two moles of acid are consumed per mole of the phosphoramide, substitution takes place with formation of acyl phosphites; the other reaction product is the amine, which combines with the excess acid[148]. If one mole of acid is used, then the substitution at the phosphorus atom is supplemented by the cleavage of the acyl phosphite by the amine and an acid cyclic phosphite is obtained[38,39,40,42,44]. A significant factor in the synthesis is its stereospecificity[38,39,44]—the formation of a labile isomer with an axial phosphoryl group. A mixture of cyclic acyloxyaminophosphoranes, capable of ready interconversion by pseudorotation, is apparently formed initially. The most stable conformer subsequently decomposes with formation of only one axial acyl phosphite. The process terminates with deacylation, which does not involve the configuration of phosphorus (see below).

The conversion of 2-amino-DOP into acid cyclic phosphites is also possible via hydrolysis accelerated by acid catalysts[7,12,114]. Sulphydrolysis takes place similarly[131].

2-Amino-DOP are also capable of insertion reactions. Thus they react with carbon dioxide to form carbamoyl phosphites, for example[136]:



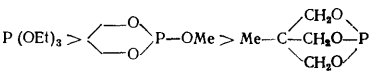


Fewer synthetic studies have been made on the conversion of neutral phosphite DOP into other compounds of this class. They can undergo selective hydrolysis[148,149] and alcoholysis[150] via the exocyclic substituent. 2-t-Butoxy-DOP [151] and its thio-analogue[152] undergo thermal decomposition to the corresponding hydrophosphoryl and hydrothiophosphoryl compounds and isobutene. According to NMR data, the equatorial substituent undergoes degradation at a higher rate than the axial substituent[151].

§ Erroneous results have been published[135].

Apart from the nucleophilic substitution at the phosphorus atom in the DOP system, radical substitution has also been described. In this case the geometrical isomers react at different rates and the process is accompanied by inversion at the phosphorus atom[153].

Addition reactions. An interesting feature of the chemical behaviour of DOP consists in the fact that the electron-donating capacity of the phosphorus atom is determined by the cyclic nature of the substances and the spatial orientation of the unshared electron pair of the phosphorus atom. At the beginning of this section we reported the characteristic features of the unshared electron pairs of the heteroatoms in DOP and in this connection one can conclude that the basicity of phosphites decreases in the sequence



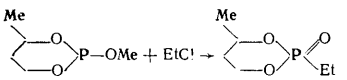
This conclusion has been confirmed experimentally. Thus the ionisation potential of the highest level of the phosphorus atom increases appreciably in this series (8.99, 9.37, 9.95 eV).[97,98] At the same time the basicity, determined both in the gas phase by ionic cyclotron resonance[154] and in the liquid phase at −50 °C from the $^1J_{P-H}$ constants of the protonated esters[155–156], decreases¶. The Lewis basicity of acyclic, monocyclic, and bicyclic phosphites varies similarly. This problem has been analysed by studying the stability of the borane[157,158] and nickel[160] complexes and by infrared spectroscopy. Advances in the investigation of the electronic structure of monocyclic DOP are also manifested by the fact that the theoretical conclusion that the basicities of differently oriented unshared electron pairs at the phosphorus atom are different has been proved experimentally: the axial pair is more basic than the equatorial pair[154,156,157,161]. Investigations demonstrating the marked influence of the exocyclic substituent on the electron-donating properties of the phosphorus atom are also of interest. Thus the amino-group significantly increases the electron-donating properties of the phosphorus atom relative to the alkoxy-group and the chlorine atom[97,98].

The study of the complex formation reactions between DOP and copper[1,162], boron[158,163], molybdenum[158,161,164], nickel[160, 165], cobalt[166,167], and palladium[168] derivatives has shown that the configuration at the phosphorus atom is retained in these reactions (X-ray diffraction has been used[158,160,161,163]). Complexes are synthesised in order to solve specific chemical problems. Adducts with the copper(I) salts are used for the identification of DOP.[1,114,162] The adducts with nickel salts[165] isomerise but-1-ene to a mixture of but-2-enes, while the corresponding rhodium[169,170] and palladium[168,171] derivatives are used as hydrogenation catalysts. In the latter case it has been shown that the configuration of the phosphorus ligand determines the activity and stereoselectivity of the catalysts. It has been stated that the formation of complexes of DOP increases their reactivity in organic synthesis[172]. Such studies are apparently very promising and merit vigorous development.

The electron-donating properties of the phosphorus atom in DOP are also manifested in their oxidation. This reaction has been widely used on a preparative scale and has involved cyclic hypophosphites[133], phosphites[7,46,48,106,145,173–179], phosphoramidites[15,48,50,158,273,180], phosphorimidites[119], phosphorocyanidites[123], phosphoroisocyanidites[126], phosphorochloridites[34], phosphorothioites[113], and phosphonites[27, 132]. The question of the stereochemistry of the oxidation reaction is being actively discussed in the literature, conflicting views being expressed. Under conditions excluding the interconversion of the different DOP formed, they are probably converted stereospecifically by the majority of oxidants into phosphoryl forms with retention of the configuration at the phosphorus atom. This is indicated by the conclusions reached in a series of studies[34,50,127,158,173,175,178, 181]. On the other hand, the possibility of the non-stereospecific oxidation has been indicated[113,176]. It has been suggested that the reactions of two geometrical isomers may not have completely identical mechanisms[182].

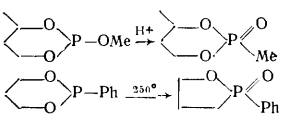
Sulphurisation†[7,25,53,106,107,113,126,133,145,175,179], selenisation [49,113,133,176,183,184], and imination[48,116,133] of DOP are carried out similarly to oxidation. Here too there is no complete unanimity in the stereochemical interpretation of the results. Both complete retention of the configuration at the phosphorus atom[127,158,179] and its partial inversion[113,176] have been noted.

Arbuzov alkylation and related syntheses. Neutral phosphite DOP undergo the usual Arbuzov alkylation[6,24,47,143,149, 162,175,187–189], for example:

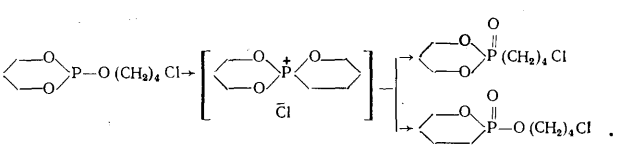


In the majority of cases the alkylation probably involves the retention of configuration at the phosphorus centre[158,162,175, 190] although its partial inversion can also occur[176]. However, one cannot rule out the possibility that the quaternisation of the DOP entails a partial inversion of the configuration of the initial substance, which in fact affects the final results. The reactivity of tripropyl phosphite has been compared with those of the corresponding dioxaphosphorinane and dioxaphospholan by differential thermal analysis. It has been shown that the reactivity diminishes in the above series[191].

The phosphite[192] and phosphonite[193] isomerisations, leading to phosphoryl compounds, are relevant to the data under discussion:



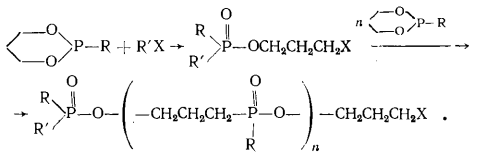
There exist data showing that the Arbuzov reaction can be accompanied by the opening of the dioxaphosphorinane system. This occurs when 2-methoxy-4,4,6,6-tetramethyl-DOP interacts with fluorosulphonic acid[194], when 2-butoxy-4-methyl-DOP interacts with bromotriphenylmethane[149], and in intramolecular interactions of the type[103,112,195]



¶ Mikolajczyk et al.[159] were the first to carry out a semi-quantitative comparison of cyclic and acyclic phosphates.

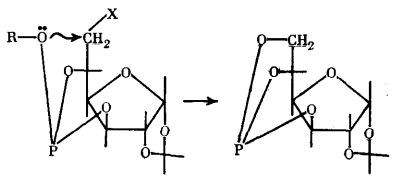
† Together with sulphurisation, other reactions involving the transfer of sulphur and occurring on treatment of elemental sulphur merit attention. Thus neutral cyclic phosphites of nucleosides are sulphurised with di-t-butyl disulphide[185] and 2-chloro-DOP is sulphurised by acetylsulphenyl chloride[156].

The competition between the endocyclic and exocyclic pathways in the decomposition of the quasi-phosphonium intermediates disappears on passing from phosphite to phosphonite derivatives. A fundamentally new method of synthesising polyphosphonates, which is impossible for acyclic systems, has been demonstrated in this instance. The method consists in treating the cyclic phosphonite with an insufficient amount of the alkylating agent. A γ-halogenopropyl phosphinate, which propagates the alkylation process via a relay mechanism, is formed in the first stage[27,196]:



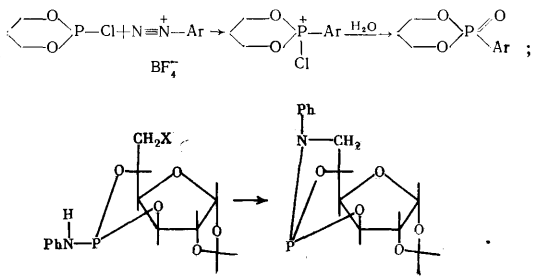
Japanese workers have reported an analogous polymerisation of cyclic phosphonites but in the presence of boron trifluoride[29].

It has recently been possible to show that the intramolecular alkylation of stereochemically rigid DOP, in which an electrophilic carbon atom and the oxygen atom of an exocyclic alkoxy-group are in close spatial proximity, can be achieved. Such spatial disposition led to a reaction which is an alternative to the Arbuzov reaction, which demonstrated the possibility of steric regulation in the alkylation of neutral phosphites#[197]:

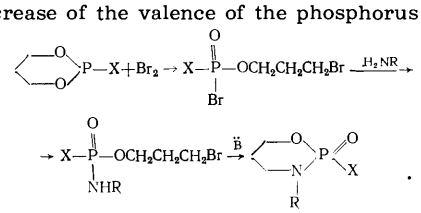


The intramolecular cyclisation of the anilide of the corresponding glycophosphorus acid takes place similarly. The possibility of the alkylation of the nitrogen atom in the amides of tervalent phosphorus acid was thereby demonstrated reliably for the first time[198] (see below).

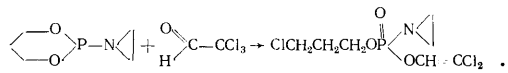
The arylation of certain DOP has also been described in the literature, for example[199]:



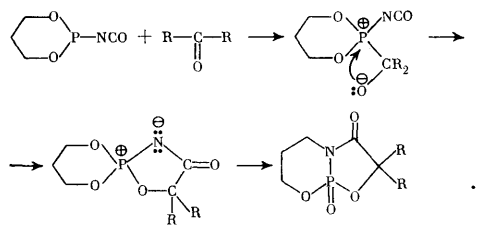
A series of reactions are related to the alkylation of DOP: interactions with hypochlorites[200], sulphenyl chlorides[188,201], and chloramines[102], which entails the formation of cyclic phosphates, phosphorothioates, and phosphoramidates. When account is taken of the stereoregularity of these reactions, conclusions can be reached concerning their preparative value. Data concerning the reactions of DOP with halogens have been published recently[111,202]. It has been established that, regardless of the type of substituent at the phosphorus atom, the reaction is accompanied by ring opening, which is unexpected. On treatment with primary amines, the acid halides formed give rise to amides, which readily cyclise. Thus here we have a transition from DOP to OAP with an increase of the valence of the phosphorus atom[202]:



The Perkow reaction also takes place with DOP, for example[203]:

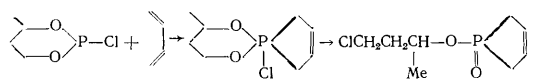


The interaction of 2-isocyano-DOP with electrophilic carbonyl compounds merits attention[204–206]:

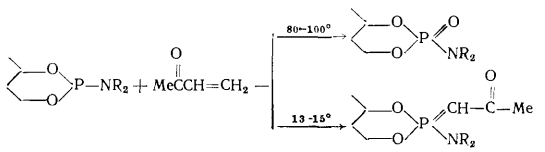


On the other hand, electrophilic carbonyl compounds with a halogen atom in the α-position react with 2-isocyano-DOP differently, namely via the Perkow mechanism, with opening of the phosphorinane ring and retention of the isocyano-group[207].

Other processes. The phosphorus atom in the dioxaphosphorinane ring is biphilic, as a result of which there is a possibility of the addition to DOP of dipolar or readily polarisable 1,3-homo- and 1,3-hetero-diene systems, for example[208]:



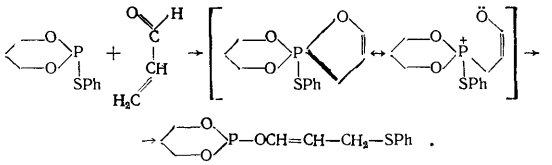
The substituent at the phosphorus atom influences the reaction significantly. Thus the amino-group prevents the addition of alkadienes. However, 2-amino-DOP can combine with polar substances, for example α,β-unsaturated ketones. Depending on temperature, different reactions take place in this instance[209]:



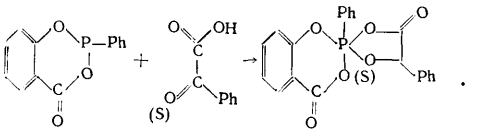
Next, the cyclic imide can react with the excess acrolein and be converted via the Wittig mechanism into 1,3-butylene phosphoramidate. It is of interest to note that 1,2-alkylene phosphoramidites react with methyl vinyl ketone to form only spiroisophospholen.

The cyclisation of the 3,5-cyclic phosphorochloridite of 6-tosyl-1,2-glucofuranose, which apparently takes place as a result of the mutual approach of the phosphorus and O(6) atoms, should also be noted[197].

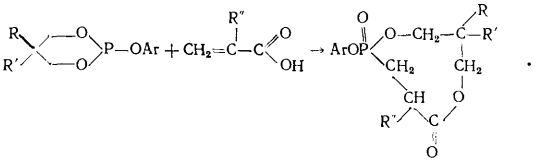
If there is an SR group at the phosphorus atom in the initial DOP, then the primary adduct reacts in an unusual manner[210]:



The cycloaddition may not be followed by a further chemical development when DOP containing the amino-group at the phosphorus atom§ or a hydrocarbon group are used, for example[212]:

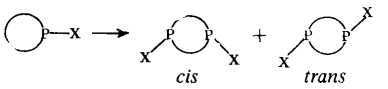


On the other hand, 2-aryloxy-DOP react with acrylic acids to form macrocyclic phosphonates[214]:

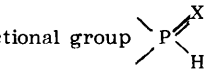


This outwardly unusual reaction has a rational explanation. The process begins with cycloaddition, after which the intermediate undergoes a reorganisation via the Arbuzov mechanism. Next, the acid cleaves the neutral phosphite to a hydrophosphoryl compound of the acyl phosphite type and the latter cyclises via a standard pathway with formation of a phosphorus–carbon atom.

An important feature of the chemical behaviour of DOP is their ability to undergo reversible condensation on storage. This process can lead to dimers, trimers, and in the general case oligomers. It is significant that the condensation leads at each stage to the appearance of pairs of isomers[215]:

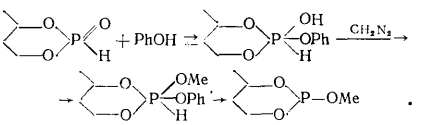


This interesting reaction was studied by NMR. According to the authors, such disproportionation is a catalytic process and is accelerated by admixtures of acid substances, frequently the hydrochlorides which usually contaminate DOP. If this is so, then disproportionation can be prevented by effective purification of the compound.

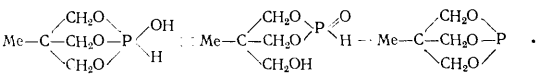
Reactions of hydrophosphoryl and hydrothiophosphoryl DOP. DOP containing the prototropic functional group  are being actively investigated, the research being accompanied by an acute controversy concerning the influence of the ring on chemical properties. Within the framework of this controversy, a special enhanced acidity has been attributed to these substances[216–219]. Reliable experiments on this subject have not been reported but it has been shown nevertheless that the hydrophosphoryl compounds in the series of DOP have certain characteristic features.

We shall consider initially the basic properties of the cyclic acid phosphites. Information on this question has been obtained in the study on the *p*-fluorophenol complexes. It has been shown that the axial orientation of the phosphoryl group ensures a higher basicity than the equatorial orientation, which is consistent with the general theoretical analysis of the systems considered at the beginning of this section. On the other hand, an approximate correspondence of the basicities of DOP and dialkyl phosphites has been established. Nevertheless the experiments performed have demonstrated a large difference between the cyclic and open-chain hydrophosphoryl compounds. The former, particularly those with an equatorial phosphoryl group, are significantly associated in solutions, while the latter are not[220]¶.

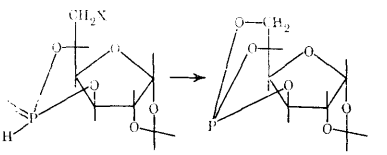
The interaction of hydrophosphoryl DOP with proton donors may apparently not consist solely in protonation. It has been shown that, after the addition of phenol or water, 1,3-butylene phosphite begins to react with diazomethane to form ultimately a cyclic neutral phosphite+[221]:



The above reaction is apparently related to the "anomalous" cyclisation of the monocyclic metriol phosphite[172,222]:



The spatial approach of the functional groups is probably an important factor in this case, since the benzyl ester of metriol phosphite also undergoes a similar cyclisation. The steric factor is undoubtedly manifested in the very easy intramolecular alkylation reactions, which are alternatives to the Michaelis–Becker synthesis[197,223]:



The reaction proceeds easily either in the presence of tertiary amines or when the substance is kept at a somewhat reduced pressure. Its chemistry resembles that of the intramolecular alkylation of bis(β-chloroethyl phosphite)[224] but takes place much more readily because the process is predetermined by steric factors owing to the rigidity of the initial system.

§ A similar final result has been noted in the case where two equivalents of electrophilic monocarbonyl compounds were used[213].

¶ The association may be accompanied by the condensation of these substances. Esters without substituents in the hydrocarbon part of the ring undergo oligomerisation particularly readily[42].

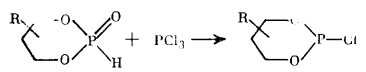
+ It has been stated that neopentylene phosphite reacts at 20–25 °C with diphenyldiazomethane to form diphenylmethyl-neopentylene phosphite, which immediately isomerises. The authors[218] attribute this observation to the anomalous acidity of the initial DOP. An alternative explanation of the experimental result is the scheme presented above.

Hydrophosphoryl DOP undergo intermolecular alkylation reactions (α-hydroxy- and α-amino-alkylation, etc.) which to a large extent correspond to the analogous reactions involving open-chain systems. We shall confine ourselves to quoting certain typical communications[225–227] and shall consider in greater detail the stereochemistry of these reactions. Soviet workers[228] were the first to show that the α-hydroxyalkylation takes place stereoselectively. Later Mosbo and Berkade supplemented this finding by data concerning the characteristics of the reaction in the presence of acids[226]. Finally, it has been shown quite recently[229] on the basis of the structure of the substances obtained that the reactions take place with retention of the configuration of the phosphorus centre. This conclusion leads to the possibility of the stereospecific synthesis of complex phosphorinanes. The kinetics of the reaction of isomeric forms of phosphorinanes with various carbonyl compounds have also been investigated and the dependence of the reaction rate on the configuration at the phosphorus atom in the initial substance has been established. This dependence is not constant for all aldehydes and ketones[229].

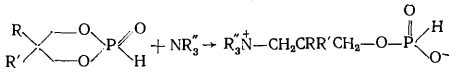
Like other acyclic analogues, hydrophosphoryl and hydrothiophosphoryl DOP can be modified oxidatively by the Todd–Atherton method as well as other procedures[5,12,110,133,230–234]. However, rigorous stereochemical features are characteristic of these substances. Thus they react stereoselectively with retention of the configuration at the phosphorus atom[117,228,235]. The problem has been discussed in greatest detail in a study[229] where both a difference between the reactivities of the geometrical isomeric forms of phosphites was demonstrated and the possible causes of the steric hindrance in the synthesis were analysed.

The report of the addition of sulphur to 1,3-alkylene phosphites[236], which takes place more readily than the corresponding reaction with dialkyl phosphites, is of undoubted interest.

Yet another valuable chemical feature of hydrophosphoryl DOP must be pointed out. It is known that, on reaction with phosphorus trichloride, dialkyl phosphites give rise to Menshutkin acid chlorides. In contrast to this, six-membered alkylene phosphites react with phosphorus trichloride retaining the fundamental molecular skeleton[237]:



Hydrophosphoryl DOP can also react with the opening of the six-membered phosphite ring. Thus, on reaction with tertiary amines, they give rise to betaines[238]:



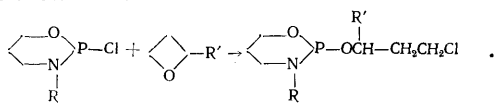
We may note that this alkylation proceeds under more severe conditions than the interaction of dialkyl phosphites with amines.

Among other reactions accompanied by a change in the six-membered ring, we shall mention cyclo-oligomerisation[42]. The presence of substituents in the hydrocarbon part of the ring prevents this process.

(b) 1,3,2-Oxaphosphorinanes

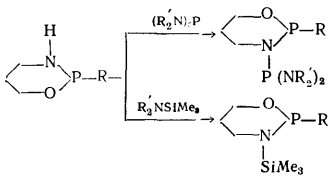
OAP have been less thoroughly investigated, but certain reactions of these compounds, which may be of interest to many specialists in the chemistry of organophosphorus compounds, have been achieved.

We shall consider initially the exchange of exocyclic substituents at the phosphorus atom. On reaction with secondary amines[57], carboxylic acid salts[60], tributyltin hydride[64], and water[239], 2-chloro-OAP exchange the chlorine atom for the corresponding groups in the usual way. The reaction with an equimolar amount of alcohol also takes place analogously[57,60,61,71,240]. We may note that the use of an excess of alcohol is inadmissible owing to the possibility of ring opening[62]. 2-Chloro-OAP are converted into esters also on treatment with oxetans[240]:



2-Amino-OAP can be made to exchange the amino-group for the hydroxy-group[239] or an alkoxy-group[57] by standard methods. In the reaction with 2-aminophenols the substitution is accompanied by addition[63].

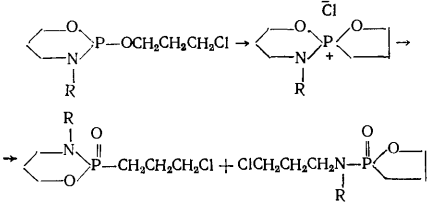
It has been shown that OAP with the endocyclic fragment $-NH-P\lessdot$ can be effectively phosphorylated[241] and silylated[70] at the nitrogen atom using mild reagents:



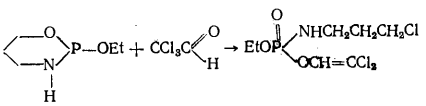
The ease of phosphorylation depends greatly on the chemical nature of the phosphoramide: the presence of electron-accepting groups at the phosphorus atom hinders the process, while the presence of electron-donating groups facilitates it[241].

OAP form complexes with transition metals, for example platinum, which are of interest for oncology[59]. OAP are oxidised[72,242] and sulphurised[67] in the usual way. The combination of the oxidation of glycerol-containing OAP with subsequent ring opening leads to a novel method of synthesis of phospholipids important for membranology[72].

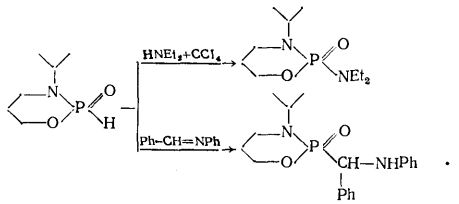
The alkylation of OAP and similar reactions have been little investigated. The intramolecular Arbuzov interaction of γ-chloroalkyl ethers of this series has been reported[240]:



The possibility of two pathways leading to the cleavage of the phosphoester bonds in the quasi-phosphonium intermediate was demonstrated in the above study. In another communication[69], devoted to the employment of the Perkow reaction for a series of OAP, only one version of the degradative stage is mentioned, which appears less probable:



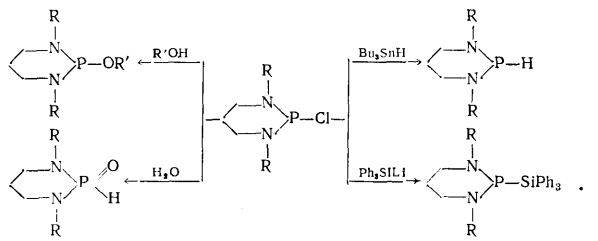
Hydrophosphoryl OAP enter into the usual oxidative phosphorylation and aminoalkylation reactions[239]:



(d) 1, 3, 2-Diazaphosphorinanes

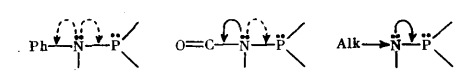
The reactions of DAP, like those of OAP, have still been little investigated, but the number of studies in this field is increasing and the scientific importance of the results obtained is growing.

A series of studies have been devoted to the substitution of the exocyclic groups at the phosphorus atom. On interaction with alcohols in the presence of bases, 2-chloro-DAP of different types give rise to ester-amides[73,75–78,81], the reaction with carboxylic acid salts produces mixed anhydrides[76,77], the reaction with tributyltin hydride affords cyclic amides of hypophosphorous acid[79,110,243], the reaction with triphenylsilyllithium leads to the formation of phosphoramidosilicides[134], and the reaction with water produces the corresponding hydrophosphoryl compounds[81,82,243]:

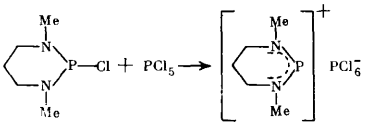


The reaction with secondary amines, which in the case of other DHP always leads to the usual results, proved to be more complex. 2-Chloro-1,3-diphenyl-DAP [78] and 2-chloro-1,3-dimethyl-4-oxo-DAP [81] react with secondary amines to give high yields of the full cyclic amides of phosphorous acid. On the other hand, 1,3-dialkyl-2-chloro-DAP behave differently in this reaction[75–77,141]. Thus the phosphorylation of aziridine and dimethylamine involves the expected nucleophilic substitution but the phosphorylation of diethylamine, which is only a little more basic, was unsuccessful. Furthermore, the attempt to synthesise the required cyclic triamide by another acid chloride method yielded an entirely unexpected result[76,77]#.

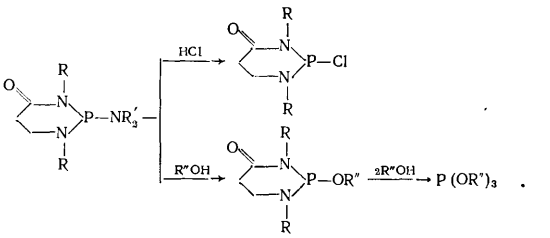
We believe that the observed difference in the phosphorylation reaction is associated with the different basicities of the expected reaction products. *N,N'*-Diphenyl derivatives and particularly compounds containing the carbonyl group are much weaker bases than the *N,N'*-dialkyl derivatives:



Compounds of the latter type therefore manifest relatively more basic properties than triethylamine and accept hydrogen chloride with the cleavage of the exocyclic P–N bond and the formation of 2-chloro-DAP. If this view is correct, then we may conclude that in the diazaphosphorinane ring there is a more pronounced electron-donating effect on the phosphorus atom than in the open-chain phosphorus tetraalkyldiamide systems. This hypothesis is confirmed to some extent by the results of a mass spectrometric study of 2-chloro-DAP and data for their interaction with phosphorus pentachloride[244]:

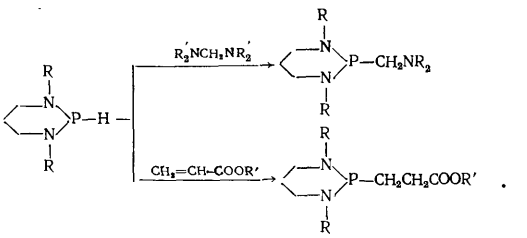


2-Amino-DAP have also been used in other substitution reactions, for example[78,81]:



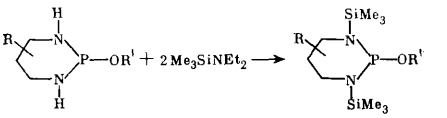
We may note that the reagents used must be measured in rigorously specified amounts, since degradation of endocyclic phosphoramide linkages is also observed in the presence of their excess.

Substitution reactions and similar processes have been described for 2-hydro-DAP:[245]



These reactions are of great interest for the synthesis of complex DAP and are apparently promising for synthetic purposes.

In conclusion of the consideration of the substitution reactions, we may point out the silylation of 1,3-dihydro-DAP at the nitrogen atom[84]:

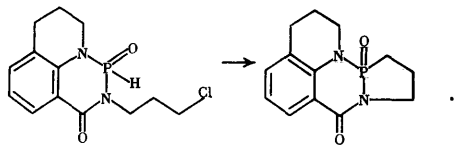


DAP tends to enter into reactions involving an increase of the valence of phosphorus: oxidation[75,77], sulphurisation[77,78], and quaternisation[244]. Unfortunately the complex-formation reactions of DAP have not yet been investigated, which impoverishes the field of the chemistry of transition metal complexes of organophosphorus ligands.

Hydrophosphoryl DAP have been relatively widely investigated. The simplest of these compounds have been made to undergo the Todd–Atherton oxidative phosphorylation[77,81,243] and aminoalkylation[77,81]. Novel possibilities for the Michaelis–Becker alkylation (including intramolecular alkylation) of

The required triamides are obtained successfully by non-acid chloride methods[77].

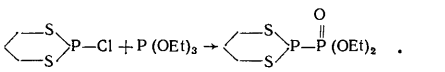
bicyclic and tricyclic DAP with formation of fairly complex systems have been recently demonstrated[83]:



(e) 1, 3, 2-Dithiaphosphorinane

DTP have been studied less thoroughly than other DHP, which, however, does not imply less chemical importance to these compounds.

Substitution reactions at the phosphorus atom have been studied mainly in relation to 2-chloro-DTP. Satisfactory results have been noted for the interactions with alcohols[86,87§], amines[87,246], mercaptans[88], and water[247]. The Arbuzov and Michaelis–Becker reactions have been carried out[248,249]:

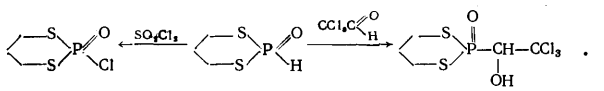


2-Amino-DTP react satisfactorily with dialkylphosphorodithioic acids to form mixed anhydrides[250]. However, they do not phosphorylate in the usual manner alcohols taken in equimolar amounts. In such cases a small amount of a secondary amine is produced and a trialkyl phosphite is obtained[87].

In contrast to other DHP, DTP are poorly oxidised and sulphurised[87,88,91,92,250]. Their complex formation reactions have not been studied.

The behaviour of hydrophosphoryl DTP merits special consideration[247]. Their physical and chemical properties differ sharply from those characteristic of other hydrophosphoryl DHP. Under the usual conditions, they are crystalline substances which are very sparingly soluble in the majority of solvents, apparently owing to their dimerisation due to their enhanced acidity.

It has been possible to achieve the chlorination and certain other reactions of these unusual hydrophosphoryl compounds, for example[247]:

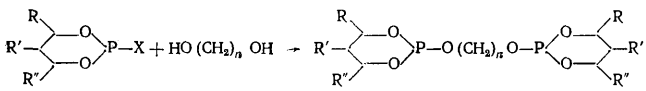


III. POLYCYCLIC DIHETEROPHOSPHORINANES

In terms of structural features, all the polycyclic DHP can be divided into three independent classes: systems with isolated rings, spirans, and condensed polycycles. Chemically, these classes are different from one another. In terms of their fundamental features, the first two resemble the monocyclic DHP and we shall therefore describe the problems of the chemistry of these substances only briefly. On the other hand, condensed polycycles are unusual systems and their synthesis and chemical properties are therefore analysed in detail in the present review.

1. Polydiheterophosphorinanes with Isolated Rings

This class of compounds has been studied only in relation to dioxaphosphorinanes. The six-membered cyclic diphosphites are of interest if only because they are more stable than their acyclic analogues. Alkylenebis-DOP have been obtained by the phosphorylation of diols with 1,3-alkylene phosphorochloridites[251], 1,3-alkylene, acyl phosphites[252], 1,3-alkylene phosphoramidites[253], or fluoroethyl phosphites[150]:



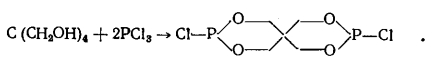
Together with the usual glycols, dihydric phenols[253] as well as systems with functional groups of substituents, for example dianhydrosorbitol[251], have been introduced into the reaction.

Among the phosphorylating agents enumerated above, amides are experimentally most convenient. These reagents have been used in the phosphorylation of novolac resins[254] and cellulose[255]. For this reason, high-molecular-weight poly-DOP have been obtained. The reactivities of di- and poly-DOP are very similar to those of the usual monocyclic compounds. They are readily oxidised and readily combine with sulphur[251,255] and are also alkylated via the Arbuzov and Perkow reactions[255].

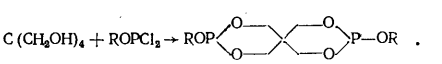
2. Spiran Bisdiheterophosphorinanes

Hitherto only dioxaphosphorinane examples of the above class of compounds have been described in the literature. Despite their structural limitations, the number of relevant studies has been fairly large. This is due to the practical importance of the spiran bis-DOP, among which polymer stabilisers[256–260] and modifiers[261], plasticisers and oils[262], antipyrenes[111], and pesticides[263] have been found.

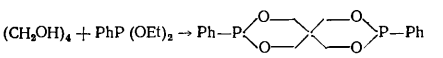
The synthesis of spiran bis-DOP is based on the employment of pentaerythritol. This readily available tetrol was made to react with phosphorus trichloride[264,265]:



Unfortunately in the published methods only a very brief description of the preparative aspect of the experiments is given and apparently they make it possible to obtain only an acid dichloride which is not altogether pure. The phosphorylation of pentaerythritol by Menshutkin acid chlorides has been described in the literature; in this case a tertiary amine must be used to bind hydrogen chloride[266]:



The second method of synthesis of a spirodiphosphite system involves the transesterification of neutral esters (usually triphenyl phosphite) by pentaerythritol for a molecular reactant ratio of 2 : 1.[18,256,257,266] Diethyl phenylphosphonite reacts similarly with pentaerythritol[37]:



The steric organisation of spiro-di-DOP has begun to be studied in a series of laboratories. By measuring the dipole moment and Kerr constants[37,267,268], NMR experiments[18],

§ The reaction with t-butyl alcohol yields a hydrophosphoryl compound and isobutene[87].

and X-ray diffraction[269], it has been shown that the molecules of these compounds contain two rings in the chair conformations, relative to which the alkoxy-group is in the axial position and the amino-group is in the equatorial position.

As regards chemical reactions, the chloride of pentaerythritol-diphosphorous acid has been studied in greatest detail. On treatment with alcohols[256,266], mercaptans[265], epoxides[211], sodium isocyanate[270], and amines[266], this compound exchanges the chlorine atom for the corresponding nucleophilic groups. The reaction with formic acid[138] or t-butyl alcohol[271] results in the formation of a bishydrophosphoryl compound, while the corresponding bisthiohydrophosphoryl compound has been synthesised by the sulphydrolysis of the corresponding acid dichloride[272].

The neutral phosphite spiro-bis-DOP and certain related compounds have been investigated in oxidation[266], sulphurisation[266,270], and Arbuzov alkylation[262,266] reactions. The last reaction has been recently proposed for the vulcanisation of fluororubbers[261].

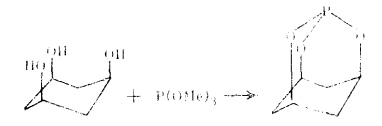
3. Condensed Polydiheterophosphorinanes

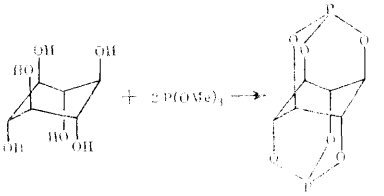
A large number of condensed poly-DHP, containing different as well as the identical structural elements, have been investigated at the present time. They can be usefully divided into four groups: 1-phospha-2,8,9-trioxa-adamantanes, 1-phospha-2,6,7-triheterobicyclo[2.2.2]octanes, and 1-phospha-2,7,8-heterobicyclo[3.2.1]octanes; the fourth group formally combines other systems which have so far been little investigated.

(a) 1-Phospha-2, 8, 9-trioxa-adamantanes

Two compounds of this group are known at the present time; phloroglucitol phosphite and scyllitol diphosphite. The molecules of these substances constitute systems bounded by dioxaphosphorinane rings in the chair conformation. This factor is responsible for the high stability of these substances and a number of their other features[273,274].

The transesterification method has been proposed to synthesise phloroglucitol phosphite and scyllitol diphosphite:





In the former case the yield is 93%[275] and in the latter only several per cent[276]. The low yield of scyllitol diphosphite is apparently due to the poor compatibility of the reactants in the phosphorylation reaction.

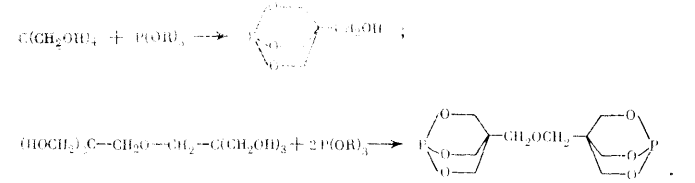
The chemical properties of the esters considered have been little investigated. It has been shown that phloroglucitol phosphite is protonated in the gas phase[154], forms complexes with palladium, platinum, nickel, copper, and silver[277], undergoes the Arbuzov reaction (it is possible to isolate the intermediate quasi-phosphonium compound),[275] and is oxidised by benzoyl peroxide to the corresponding phosphate[278]. The reaction of this phosphite with ozone has also been studied[274]. Finally, the hydrolysis of 1-phospha-2,8,9-trioxa-adamantane, consisting in the cleavage of one of the ester linkages with formation of a bicyclic hydrophosphoryl compound which forms metal complexes activating the phosphorus centre in nucleophilic reactions, has been considered in the literature[272].

(b) 1-Phospha-2, 6, 7-triheterobicyclo[2. 2. 2]octanes

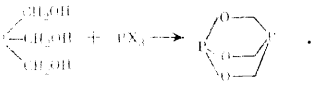
This is the most numerous and most thoroughly investigated group of compounds among all the condensed poly-DHP. It includes phosphite, phosphorothioite, and phosphoramidite systems, which have a number of characteristic features. Unfortunately the extent to which the above types of bicyclic compounds have been studied are different and so far it is difficult to achieve a thorough comparison of their properties.

1-Phospha-2,6,7-triozabicyclo[2.2.2]octanes have been synthesised by the phosphorylation of 1,1,1-tris(hydroxymethyl)alkanes and related compounds. Phosphorus trichloride[279,280], the simplest neutral phosphites[281–283], phosphorous acid triamides[281], and acyl phosphites[252] have been used as phosphorylating agents. The simplicity of the methods of synthesis of these compounds and also the ready availability of the initial triols explain the interest of chemical engineers in 1-phospha-2,6,7-trioxabicyclo[2.2.2]octanes, particularly in the possibility of using them as stabilisers for different materials[281].

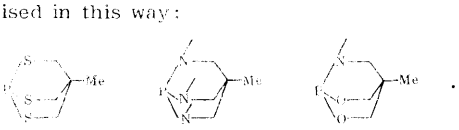
Pentaerythritol[266,279] and bispentaerythritol[285] are phosphorylated analogously, forming skeletal systems:



The above reactions have been extended in recent years to the phosphorylation of tris(hydroxymethyl)phosphine, which yielded the phosphinophosphite 1,4-diphospha-2,6,7-trioxabicyclo[2.2.2]octane[286]:



In addition, similar condensations have been achieved with tris(mercaptomethyl)ethane[287], tris(methylaminomethyl)ethane[183,288,289], and bis(hydroxymethyl)methylaminomethylethane[289]. Bicyclic phosphorinanes containing sulphur and nitrogen have been synthesised in this way:



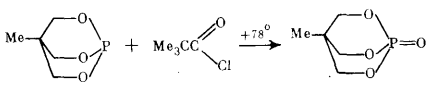
Finally, 2,3,5,6,7,8-hexazabicyclo[2.2.2]octane, which is based on an inorganic skeleton, has been obtained from 1,2-dimethylhydrazine[288].

Structurally, phosphatriheterobicyclo-octanes are in many respects analogous to the phosphatrioxa-adamantanes examined above—in each individual instance the bulky molecules of the substances are bounded by 1,3,2-diheterophosphorinane

rings, which differ from one another. Thus the bonds are significantly eclipsed in phosphatriheterobicyclo-octanes, which results in different mutual orientations of the bonds of the P–O–C–H vicinal system in their molecules[273]. The spectroscopic properties of the complexes of the above compounds have been compared[273]. We shall now consider the chemical behaviour of 1-phospha-2,6,7-triheterobicyclo[2.2.2]octanes. The corresponding 2,6,7-trioxa-derivatives have been studied in greatest detail. They are appreciably weaker based than the monocyclic DOP and phosphatrioxa-adamantane. This conclusion is based on the study of the ionisation potentials by photoelectron spectroscopy[97,99,290], the proton affinities in the gas phase (ion–cyclotron resonance)[154], the stability of the complexes with phenol[291], and the spectroscopic properties of protonation products[156,158,292] and the borate[155] and nickel[160] complexes. All these data indicate a relatively pronounced s character of the unshared electron pair of the phosphorus atom in 1-phospha-2,6,7-trioxabicyclo[2.2.2]-octanes. Nevertheless these phosphites form complexes readily with many metals: copper and silver[277,293], molybdenum[164], manganese[294], rhenium[295], cobalt[166,167,296,297], nickel[165,296,298], iron[296,299,300], and platinum and palladium[277, 301].

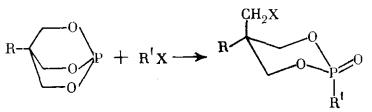
Some of the complexes enumerated above are of particular importance as stabilisers of olefins[164] or catalysts of the isomerisation and oligomerisation of unsaturated compounds[165, 302–304].

1-Phospha-2,6,7-trioxabicyclo[2.2.2]octanes are oxidised in the usual way to phosphates[266,278,279,305]. Several new observations have been made for this reaction, which has been thoroughly investigated in a series of neutral phosphites: it has been noted that hydrogen peroxide[279] and pivaloyl chloride[306] can be used as oxidants:

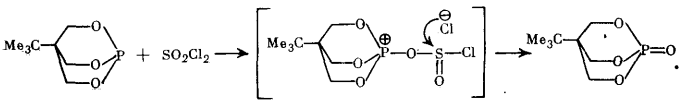


It has been established that metriol and etriol phosphites react with ozone to form stable ozonides, which decompose on heating with the corresponding bicyclic phosphates and singlet oxygen[274,305]. It was concluded that such ozonides are likely to be of preparative value[305]. Sulphurisation[266,307, 308], selenisation[308], and imination[286] have been studied together with oxidation.

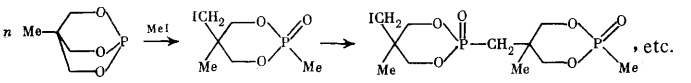
The above neutral phosphites exhibit stereoselectivity in alkylation by the Arbuzov reaction[275]:



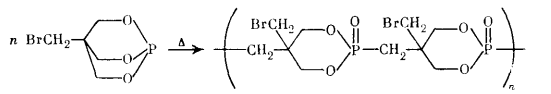
The reactions with sulphenyl chlorides[309], chloramines[309,310], bromine[172], chlorine, and sulphuryl chloride[172,309,310] proceed analogously. In the last case the possibility of a different reaction pathway was noted when a bicyclic phosphite with a tertiary butyl group in the C(4) position was used. This bulky group prevents the traditional attack by the anion on the key carbon atom and its attack is therefore directed to the sulphoxy-group with the ultimate formation of a neutral phosphite, i.e. oxidation takes place[311]:



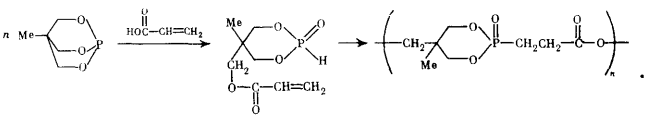
The Arbuzov and related reactions have been suggested for the synthesis of non-combustible phosphorus-containing polymers. Thus the reaction of metriol phosphite with a catalytic amount of methyl iodide results in the formation of a polyphosphonate[312]:



Another polyphosphonate has been obtained in the autoalkylation of bromometriol phosphite[280]:



Pentaerythritol phosphite polymerises similarly and the resulting polyphosphonate hydrolyses to β,β,β-tris(hydroxymethyl)ethylphosphonic acid[313]. The copolymerisation of metriol phosphite with acrylic acid is of interest[314]:



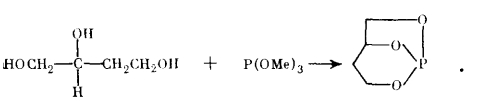
Much attention has been devoted in the literature to the hydrolysis of 1-phospha-2,6,7-trioxabicyclo[2.2.2]octanes and it has been shown that these substances are more resistant to hydrolysis and acidolysis than the usual neutral phosphites[41]. However, it has been possible to achieve the hydrolysis of metriol phosphite[172] and pentaerythritol phosphite[315]. In the former case the isolation of the hydrolysis products involves considerable difficulties and it has therefore been suggested that the reaction mixture be subjected to complete silylation with formation of two silyl phosphites[172]. Bicyclic phosphites are apparently not hydrolysed by the traditional Arbuzov mechanism, which emphasises yet again their unusual chemical behaviour.

Phosphabicyclo-octanes containing nitrogen instead of oxygen have so far been little investigated and data required for a reasoned comparison of their nature with that of the related systems are still being merely accumulated. Nevertheless we may point out that the results of an X-ray diffraction study[288], the dipole moments and NMR spectra[316], and photoelectron spectroscopic data[317] have been described. Oxidative[183], imination[318], and complex formation[319] reactions have been achieved.

(c) 1-Phospha-2, 7, 8-triheterobicyclo[3. 2. 1]octanes

The study of this series of compounds was begun with the simplest phosphite and was later extended to complex phosphorylated hydrocarbons.

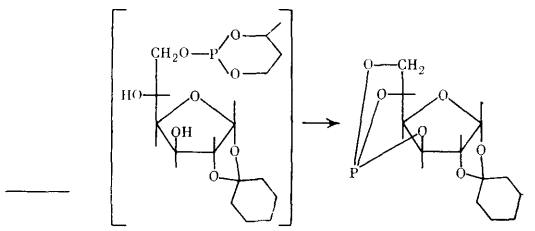
1,2,4-Trihydroxybutane and its 2,2-dimethyl derivatives are readily phosphorylated by phosphorus trichloride[320], trimethyl phosphite[320,321], or phosphorus hexaethyltriamide[284,320] with formation of 1-phospha-2,7,8-trioxabicyclo[3.2.1]-octanes, for example:



The structure and conformation of the phosphites have been investigated by ^{1}H NMR.[18,322]

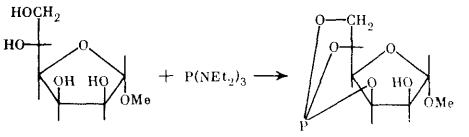
In later studies it was shown that 1,2-alkylideneglucofuranoses, whose molecules incorporate a 1,2,4-triol fragment are phosphorylated similarly to phosphorous triamides[284],

[323] and triphenyl phosphite[324]. The intramolecular transesterification



which takes place readily at 20 °C, constitutes a very novel synthesis[325]. The structure of such compounds has been demonstrated by X-ray diffraction[326], ^{1}H NMR, and ^{13}C NMR.[234]. An important outcome of this investigation was the establishment of a significant decrease of the OPO valence angles compared with the usual values.

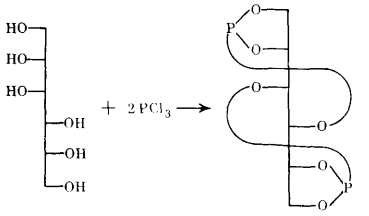
Apart from the carbohydrate triols mentioned above, a series of corresponding tetraols have been introduced into the reaction with phosphorus hexaethyltriamide and it was shown that, when the hexafuranose molecule contains hydroxyls in the C(3), C(5), and C(6) positions with the "glucose configuration", then these hydroxyls (and not the fourth hydroxyl) actually react[327]. This can be illustrated by the following synthesis:



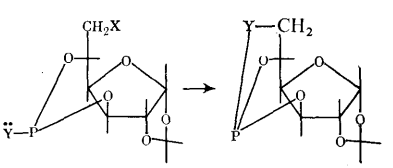
The data presented permit the conclusion that the 1-phospha-2,7,8-trioxabicyclo[3.2.1]octane system, adapted to the structure of hexafluranoses, exhibits a special stability.

6-Alkyl(aryl)amino-6-deoxy-1,2-isopropylideneglucofuranoses, 3-benzamido-3-deoxy-1,2-isopropylideneglucofuranoses[328], and the corresponding mercapto-derivatives[329, 330] are phosphorylated analogous to the sugars mentioned above. A series of 1,2-isopropylideneglucofuranose derivatives of bicyclicphosphoramidites and bicyclicphosphorothioites were synthesised.

A more complex case of phosphorylation was noted in the interaction of a hexaol (sorbitol) with phosphorus trichloride. A bisbicyclicphosphite, whose molecules contain two 1-phospha-2,7,8-trioxa[3.2.1]octane fragments, was isolated as one of the products[331]:

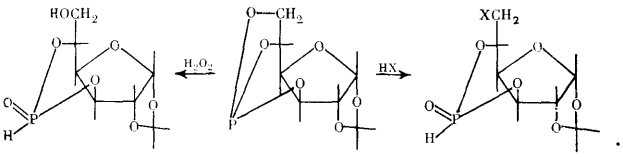


A second method of synthesising bicyclicphosphites, bicyclicphosphoramidites, and bicyclicphosphorothioites derived from 1,2-alkylideneglucofuranoses consists in stereocontrolled condensations[197,198,330]:



As regards chemical reactions, the 1-phospha-2,3,7-trioxabicyclo[3.2.1]octanes considered are characterised by important features determined by their molecular geometry, namely by the decrease of the OPO valence angles contrary to the usual behaviour. As a consequence of this decrease, the amount of *s* character of the unshared electron pair of the phosphorus atom greatly increases, which reduces in its turn the basicity and nucleophilicity of this atom. The foregoing has been confirmed experimentally by comparing the Lewis basicities[160] and by protonating in the gas and liquid phases[154,156] various neutral phosphites. It is noteworthy that 1-phospha-2,3,7-trioxabicyclo[3,2,1]octanes are not oxidised by powerful oxidants[320,323,325], do not combine with sulphur[323], and undergo the Arbuzov alkylation with much difficulty[320,324,325]. On the other hand, they are very readily halogenated by chlorine and bromine[323]. The reaction proceeds via a stage involving the formation of an adduct with a pentacovalent phosphorus atom[323]. The very mild interaction with chloramines apparently proceeds in the same manner[320].

The bicyclic phosphites considered do not react with the usual strong acids, but readily undergo ring opening on treatment with hydrogen chloride and particularly hydrogen bromide in a non-polar medium and also on treatment with hydrogen peroxide[197]:

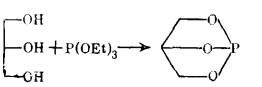


We may point out that other types of DHP are oxidised by hydrogen peroxide without ring opening, i.e. we may note instances of a significant influence of the geometry of the phosphite on its reactivity.

1,2-Alkylideneglucofuranose cyclicphosphoramidites and cyclicphosphorothioites have been little investigated. It has been shown that they readily undergo methanolysis with formation of trimethyl phosphite and the corresponding sugar [328,329,330]. The chlorination of phosphorothioites is of interest[329,330].

(d) Other Condensed Polydiheterophosphorinanes

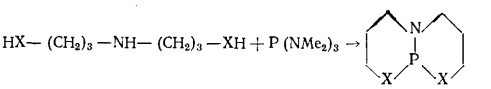
It was shown that the transition from 1-phospha-2,6,7-trioxabicyclo[2.2.2]octanes to 1-phospha-2,7,8-trioxabicyclo-[3.2.1]octanes entails a decrease of the OPO valence angles and hence a significant alteration of the chemical properties of the substances. An even greater deformation of the phosphite valence angle should occur in 1-phospha-2,6,7-trioxabicyclo[2.2.1]heptanes. The simplest compound of this series has been synthesised by phosphorylating glycerol with triethyl phosphite[332]:



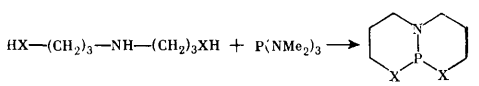
The structure of this substance has been recently confirmed by electron diffraction and it was shown that the C–O and P–O bonds in the bridged structure are longer than in the phosphorinane structure[333]. From this follows the conclusion that the bridge fragment is chemically more labile in reactions involving the opening of the cyclic system. However, this conclusion conflicts with data present in a communication[334] where the opposite opening of the bicyclic compound in the reaction with phosphorus trichloride is reported.

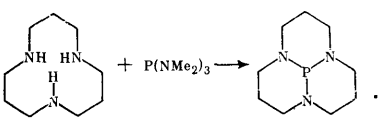
The OPO valence angles in the bicyclic glycerol phosphite are contracted compared with the angles in the bicyclic compounds examined above[333]. As a result of this, the bicyclic glycerol phosphite is a very weak nucleophile[278].

Unusual structural motifs may be manifested in the formation of condensed DHP whose molecules contain tervalent nitrogen atoms. The linear secondary aminodiols[335] and triamines[336] give rise to unusual bicyclic DHP on interaction with phosphorus triamides:



Tris(1,3-propylene)triamine is phosphorylated analogously[337]:





This reaction has been extended also to cyclic triamides[336,338].

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Summarising, we may note two principal conclusions. The first concerns the availability of the substances considered and consists in the fact that at the present time simple methods have been proposed for the synthesis of various types and classes of DHP. This has led to a significant expansion of the synthetic and structural possibilities in the chemistry of tervalent phosphorus and a firm base has been created for the solution of problems of practical importance.

The second conclusion concerns the reactivity of DHP. The high synthetic value of DHP has been demonstrated and the fundamental differences between them and the corresponding acyclic derivatives have been established. It is known that dialkyl phosphorochloridites and phosphoramidites, as well as compounds of a similar type tend to disproportionate and satisfactory results have not therefore been obtained in all the reactions. The above factor as well as the unusual conformational features of DHP facilitate more promising quantitative studies of the reactivities of these compounds compared with their acyclic analogues. DHP can apparently be more correctly employed in the study of the electronic effect of substituents linked to the tervalent phosphorus atom and of other urgent problems of physical organophosphorus chemistry.

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The Unpaired Electron in Transition Metal Complexes

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The present state of research into complex and organometallic compounds with an unpaired electron is described. Paramagnetic complexes of transition metals, differing in the position of the free-radical fragment and in the nature of the paramagnetic ligands are examined. The possibility of investigating the intramolecular electron transfer in the metal-ligand system and the formation of intermediate free-radical products in reactions of transition metal compounds is discussed.
The bibliography includes 201 references.

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I. INTRODUCTION

The study of transition metal complexes carrying an unpaired electron presupposes two interrelated aspects. Firstly, the study of the possibility of intramolecular electron transfer in the metal–ligand system. Secondly, the elucidation of the question of what changes are undergone by the free radical while it is coordinated in the sphere of the metal. The first aspect is of interest in connection with the fact that there should exist an analogy between macromolecular biological systems responsible for electron transport and artificial models in which such transport is possible. The transition metal, capable of existing in various oxidation states, may play a decisive role in electron transport. On the other hand, the coordination of a free radical leads to a change in its fundamental characteristic, namely its reactivity. Furthermore, the free radical undoubtedly influences the electronic structure of the molecule of the complex.

The solution of the above problems has become possible as a result of the development of spectroscopic methods for the investigation of paramagnetic organometallic compounds. These compounds can be divided into three main types:

(1) Paramagnetic compounds whose properties are determined by the paramagnetism of the central metal ion, i.e. the so-called spin-unpaired complexes.

(2) Charged paramagnetic systems—radical-anions and radical-cations generated by one-electron reduction or oxidation and neutral radicals formed on photolysis, radiolysis, or chemical bond dissociation.

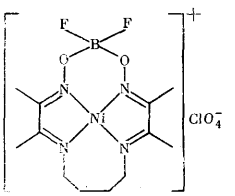
(3) Complexes with paramagnetic ligands.

Like any classification, such subdivision is to some extent arbitrary. Strictly speaking there exist two clearly distinguished limiting cases—transition metal complexes with an odd number of electrons in the *d* level and complexes with an unpaired electron located on the periphery of the ligand and virtually incapable of hyperfine interaction with the metal nucleus. Intermediate compounds are of greatest interest. In systems where there is a possibility of the delocalisation of an electron over the entire molecule, one may expect the occurrence of intramolecular electron transfer, which determines the functional similarity of such compounds with oxidation-reduction coenzymes.

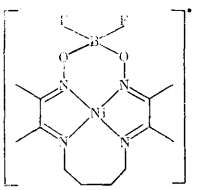
An example of intramolecular electron transfer is provided by the process occurring in the cofactor NAD (nicotinamide-adenine dinucleotide). The reduction of the cation NAD^+ leads to NAD·. Kinetic data have shown[1] that in the initial stages an electron adds to adenine and is then rapidly transferred to the nicotinamide component of the molecule, a signal due to the nicotinamide radical appearing in the EPR spectra. This mechanism has been proposed by analogy[2] for biological systems containing a transition metal ion. Intramolecular electron transfer has been postulated for cytochrome *c*, the one-electron oxidation of which results in the formation of the ferrocytochrome *c* radical-cation (the unpaired electron is localised in the porphyrin ligand). There is then rapid electron transfer within the molecule with participation of the iron atom and ferrihaemoprotein is formed[2]:

$$Fe^{II}Cyt\text{-}c \xrightarrow{-e} [Fe^{II}Cyt\text{-}c]^{\ddagger} \rightarrow Fe^{III}Cyt\text{-}c \ .$$

An interesting case of intramolecular electron transfer *in vitro* has been noted recently[3]; the nickel(II) complex



was obtained, its reduction by a one-electron reductant (cobaltocene) yielding a one-electron reduction product:



Two signals were observed in the EPR spectrum of this product in the frozen liquid-crystal phase: the first (g = 2.113) was assigned to a complex containing a paramagnetic nickel(I) ion and the second (g = 2.048) was

assigned to a radical-anion containing nickel(II). Thus there are two complexes in the first of which the unpaired electron is localised at the central nickel ion and in the second it is localised in the organic ligand. In other words the one-electron reduction of the nickel(II) complex with a macrocyclic ligand leads to the formation of two extreme forms of the reduced product, which are in equilibrium:

$$Ni^{II}(L^{\cdot-}) \underset{}{\overset{K=0.27}{\rightleftharpoons}} Ni^{I}(L) \ .$$

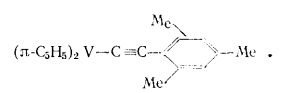
This example is an unusual instance of electronic tautomerism in solution and demonstrated the possibility of the artificial generation of metal-containing systems capable of effecting the intramolecular electron transfer. The search for and study of such systems may provide a key to the understanding of the most important catalytic and biochemical processes in which the transition metal and its chemical environment play a decisive role.

II. TRANSITION METAL COMPLEXES CONTAINING A PARAMAGNETIC CENTRAL ATOM

The first EPR data for paramagnetic transition metal complexes were obtained in 1957 [4,5] in studies of complex formation reactions. The method is applicable only to compounds containing a transition metal atom with an odd number of electrons in the *d* or *f* levels. The paramagnetism of the complexes is determined in this instance by the properties of the central ions with d^1, d^3, d^5, d^7, d^9, and f^7 configurations. Since numerous reviews and monographs have been devoted to studies of such complexes[6-14], they will not be considered in the present review. We should like to mention merely that the unpaired electron in such complexes may interact with the ligand environment. Fairly high constants for the hyperfine interaction (HFI) of the unpaired electron with the nuclei of the coordinating ^{14}N or ^{31}P atoms are characteristic of ligands containing heteroatoms (pyridine, isoquinoline, pyrazole, imidazole, triphenylphosphine, etc.).[15-17]

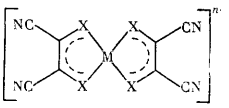
It has been shown[16] that the degree of delocalisation of spin density over the ligand depends on the geometry of the complex and increases on passing from an octahedral to a tetrahedral structure. The spin density can be delocalised via both π and σ metal–ligand bonds[18-21]. For π-complexes of the sandwich type, the interaction of the metal *d* orbitals with the π-electron system of the ligand leads to HFI with the ring protons; for example $a_H = 3.8$ G has been obtained for dinaphthalenevanadium(0).[22,23]

Cases of the formation of organic σ-complexes, in which a π-type transfer of spin density takes place, are also possible; for example, this happens in the following organometallic radical containing two unpaired electrons[24]:



The degree of delocalisation of the spin density to the acetylenic ligand is significantly greater than to the π-cyclopentadienyl ligands.

However, in many instances it is fairly difficult to establish the factor which determines the paramagnetism of the molecules of the complex. A change in the oxidation state of the metal in complexes, associated with the appearance of an odd number of electrons in the *d* level, can be achieved by the one-electron reduction (or oxidation) of the corresponding initial compounds. However, this entails the reduction (or oxidation) of the molecule as a whole and the change in the effective charge of the metal by unity is not an obligatory consequence of the process[25-33]. Thus the electrochemical reduction of the nickel-subgroup metal dithiolate complexes yielded the corresponding d^9 complexes:

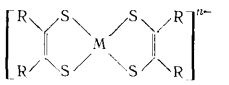


M = Ni, Pd, Pt; X = S, NH_2, $n = 1, 2$

It is believed[25] that the main process involves the one-electron reduction of the metal:

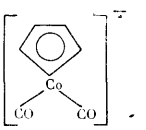
$$M^{II} \xrightarrow{-e} M^{I} \ .$$

The oxidation state of five, which is unusual for platinum and palladium, is attributed by the above investigators to the oxidised form of the dithiolene complexes of the quadrivalent metal formed in the reaction with bromine[26]:



M = Pd, Pt; R = CN, $n = 1, 2, 3$;
R = H, Alk, Ar, CF_3, $n = 0, 1, 2$.

The radical-anion of (π-cyclopentadienyl)cobalt(I)-dicarbonyl, formed as a result of γ-irradiation, has been called[30] a cobalt-centred radical:



A number of studies[31-33] have been made on the oxidised form of cobalt complexes with macrocyclic ligands, which are structural models of vitamin B_{12}. EPR data suggest that the central cobalt(II) ion is paramagnetic.

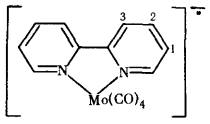
In the general case the possibility of the delocalisation of the spin density over the entire molecule is influenced by the nature of the metal–ligand bond[34-42].

The electronic "conductivity" of substrates depends not only on the nature of the metal but also on its ligand environment and is a characteristic property of enzyme-like molecules. The study of metal complexes with ligands capable of undergoing ready and reversible one-electron transitions, involving only partly the valence shell of the metal, is particularly promising in this connection.

III. CHARGED AND NEUTRAL PARAMAGNETIC COMPLEXES

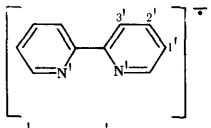
The first attempts to obtain and investigate organometallic radical-anions and radical-cations were made in the 1960's. At that time a series of communications by Dessy and coworkers[43-58] were published, describing the generation of charged paramagnetic species by the electrochemical oxidation (or reduction) of organometallic compounds. The study of the radical-anions of a series of chromium, molybdenum, tungsten, iron, and ruthenium complexes by various physicochemical methods enabled the authors of the above studies to reach conclusions, firstly, concerning the degree of delocalisation of the spin density by means of EPR studies, secondly, about the charge distribution (with the aid of the NMR method), thirdly, about the nature of the electric field gradient at the metal atom nucleus (with the aid of the Mössbauer method), and, fourthly, about the transmission of charged density via the metal atom (with the aid of infrared spectroscopy).

The constants for the hyperfine interaction of the unpaired electron with the ^1H and ^{14}N nuclei of bipyridyl coordinated in the bipyridylmolybdenum tetracarbonyl radical-anion and in the radical-anion of the free ligand have been compared[44]. The HFI constants (a, G) are smaller for aromatic protons in the radical-anion of the complex, while the constant for the HFI with the coordinating ^{14}N heteroatoms increases on passing from the free ligand to the complex. This permitted the conclusion that the organometallic group exhibits an electron-accepting effect in the redistribution of spin density.



$a_H^1 = 3.96$; $a_H^2 = 0.67$

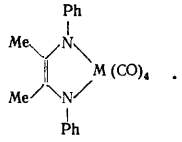
$a_H^3 = 1.2$; $a_N = 3.96$



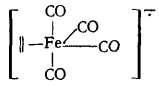
$a_H^{1'} = 4.96$; $a_H^{2'} = 0.7$

$a_H^{3'} = 1.4$; $a_N' = 2.48$

The change in charge density at the atoms of the organic ligand relative to the free ligand was estimated by NMR from the decrease in the chemical shift $\Delta\delta$ of the aromatic carbon atoms in the chromium, molybdenum, and tungsten complexes[57]:



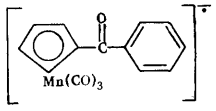
It was found that the charge is almost wholly localised at the metal atom. Mössbauer spectroscopic data confirmed the increase of electron density at the metal atom following the formation of a complex. It has been shown in relation to olefin complexes of iron that the spin density is mainly concentrated in the ligand:



Mössbauer spectra yield a lower σ-electron density on the nucleus of the iron atom, which is due to the increase of the s-electron shielding caused by the ligand → metal π-electron donation. Electronic absorption spectroscopic data have shown that the electron occupies the π^* orbital of the ligand, but most of the charge is "withdrawn" via the metal to the carbonyl groups[45].

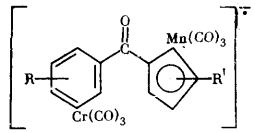
Thus the coordinated ligand in the L–M–CO system is an effective spin reservoir but a weak charge reservoir, i.e. the spin and charge are separated in the charged radical systems.

Chromium and manganese carbonyl complexes with ligands of the cyclopentadienyl and arene types have been investigated[59–61]. The benzoylcyclopentadienylmanganese tricarbonyl radical-anion has been obtained by reduction with metallic potassium:



Its EPR spectrum consists of six equal-intensity lines with $a_{^{55}Mn} = 7.68$ G. Each component of this sextet is split into a doublet (2.91 G) of triplets (1.03 G), which indicates the involvement of the ligand in the delocalisation of the spin density.

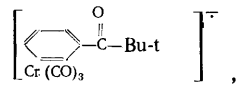
The electronic effects have been investigated for a series of substituted radical-anions obtained by the reduction of neutral complexes with metallic potassium in dimethoxyethane:



R = H, *o*-Me, *m*-Me, *p*-Me, *p*-OMe;
R' = H, α-Me, β-Me.

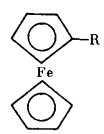
Signals due to the hyperfine interaction with the ^{55}Mn and ^{53}Cr nuclei and with the ligand protons have been observed in the EPR spectra of such radical-anions, $a_{^{55}Mn}$ depending on the positions of the substituents R and R'; the g-factor varies in the range 1.9989–2.0002; the constants $a_{^{55}Mn}$ range from 1.62 to 5.11 G; the constant a_{p-H} for the ligand protons is in the range 1.53–1.65 G, while a_{o-H} is in the range 0.78–2.70 G. Studies of the EPR spectra indicate an appreciable delocalisation of electron density over the entire chromium–benzoylcyclopentadienyl–manganese system, which can be accounted for solely by taking into account the appreciable π-overlap between the metal and ligand orbitals and also by the π-electron conjugation with the aromatic system.

Comparison with the benzoylcymantrene radical-anion described above makes it possible to elucidate the principal effect of the $Cr(CO)_3$ group—the delocalisation of the spin density over the entire system, including the $Mn(CO)_3$ group. The conclusions reached agree with the results of studies of the complexes by ^1H NMR and infrared spectroscopy[62–69]. In the arene complex of chromium with a t-butyl substituent at the carbonyl group[64],



it was not possible to observe the hyperfine interaction with the ^{53}Cr nucleus, as in the case of the carbonyl complexes $(CO)_5MC(R)Ph$, where M = Cr, Mo, or W and R = OMe or Ph.[65]

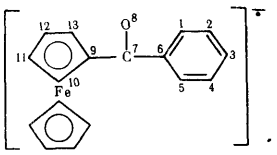
A large series of studies have been devoted to metallocenes, starting with the simplest representatives of compounds of this class—ferrocene[66] and its derivatives[67–72]:



R = Bz, CC_6H_4Me (O), NO_2, C_6H_4CN, CC_6H_4COOMe (O), $C_6H_4NO_2$.

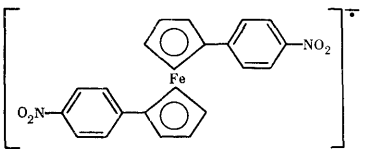
Comparison of the results of the calculation by the Hückel molecular orbital method with the observed hyperfine structure of EPR spectra[68] yields a quantitative distribution of the spin density in the radical-anion. Overall, the ferrocenyl group is destabilising compared with the phenyl group. In the presence of both groups in one molecule, the degree of delocalisation of the spin density is greater

in the direction of the benzene ring[69]:



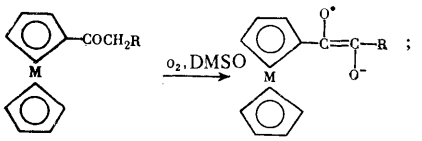
The following values have been obtained for the phenyl group: $a_H^1 = 3.3$ G; $a_H^5 = 2.91$ G; $a_H^2 = a_H^4 = 0.89$ G; $a_H^3 = 4.3$ G. In the ferrocenyl group the delocalisation involves only one cyclopentadienyl ring ($a_H^{10} = a_H^{13} = 0.89$ G).

In complexes with *p*-nitrophenyl substituents of the type

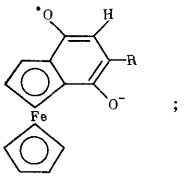


the unpaired electron is located almost wholly in the nitrophenyl fragment by virtue of the high electronegativity of the nitro-group ($a_N = 10$ G, which is close to the value for the nitrobenzene radical-anion), while the constants for the HFI with the protons of the cyclopentadienyl rings are small ($a_H \leq 0.3$ G).[67]

Stable paramagnetic semiquinones of the metallocene series are formed on oxidation of ketones containing the α-methylene group[70,71]:



M = Fe, Ru; R = Me, Et, iso-Pr, iso-Bu, Ph;
a_H(ring) = 0.57 G, a_H(Me) = 3.4–4.4 G.



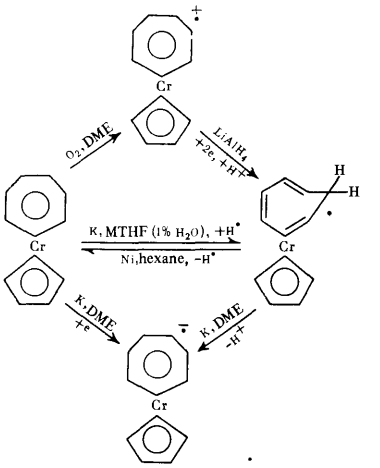
R = H, Me, Et, iso-Pr; a_H(ring) ≅ 0.4 G, a_H = 4.05 G, a_H(Me) = 3.47 G, a_H(Et) = 3.54 G, a_H(iso-Pr) = 3.35 G.

The ease of the one-electron oxidation of metallocene derivatives is confirmed by the formation of paramagnetic salts, where the anionic component may consist of the radical-anion derived from the organic one-electron acceptor tetracyanoquinodimethane (TCNQ):[73]

$$\{[Fe(C_5Me_5)_2]^+\}_2(TCNQ)_2^{2-}.$$

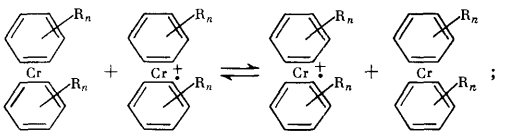
Such salts are in essence organometallic analogues of charge-transfer complexes.

An interesting cycle of one-electron transitions has been described for π-cycloheptatrienyl-π-cyclopentadienyl-chromium[74–76]†:



Lines due to the HFI of the unpaired electron with the ^{53}Cr nucleus have been observed in the EPR spectra of paramagnetic complexes of chromium ($a_{^{53}Cr} = 17.35$ G for the radical-anion, $a_{^{53}Cr} = 19.0$ G for the radical-cation, and $a_{^{53}Cr} = 19.7$ G for the radical). A change in $a_{^{53}Cr}$ is observed also for arene complexes of chromium[75].

The electron exchange in the arene π-complexes of chromium and their deuterated analogues has been investigated by EPR and ^1H NMR; the rate constants for the exchange have been measured and the influence on the latter by various substituents has been investigated[77,78]:



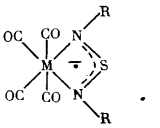
R_n = Me, 1,3-Me_2, 1,3,5-Me_3, 1,2,4,5-Me_4.

Paramagnetic complexes of chromium, molybdenum, and tungsten are formed also in the one-electron reduction of carbonyl complexes containing sulphur diimides as bidentate ligands[79]:

$$\{(CO)_4M[S(NR)_2]\}^{\bullet-};$$

R = t-Bu, Ph, 4-MeC_6H_4, 4-$O_2NC_6H_4$.

Analysis of the EPR spectra, calculations by the ENDO method, and comparison with the spectra of the radical-anions of the initial ligands $[S(NR_2)]^{\bullet}$ have led to the conclusion that the unpaired electron is localised in the ligand:



The radical-anions obtained are fairly stable; for example, the half-life of the chromium complex is 6 min.[79].

Cationic paramagnetic complexes of chromium containing carbenes as ligands can be obtained by one-electron oxidation. These paramagnetic compounds have been isolated as tetrafluoroborates[80].

The formation of radical-anions in the electrochemical reduction of clusters has been reported. Radical-anions have been generated from iron carbonyls and also from their ruthenium and osmium analogues[81]:

$$[Fe(CO)_{12-n}L_n]^{\bullet-}$$

L = PPh_3, $P(OMe)_3$, $P(OPh)_3$, etc.

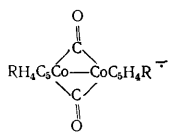
†In the formula below DME = 1,2-dimethoxyethane and MTHF = 2-methyltetrahydrofuran (Ed.of Translation).

The radical-anions of a tricobaltcarbon cluster have been obtained by electrochemical reduction[82]:

$$YCCo_3(CO)_9 \xrightarrow{+e} [YCCo_3(CO)_9]^{\cdot-} ;$$
$$Y = H, Me, Et, F, CF_3, CF_3CH_2, Cl, Br, Ph, p\text{-}FC_6H_4, COOH, p\text{-}HOC_6H_4, Me_3Si, \alpha\text{-}C_{10}H_7 .$$

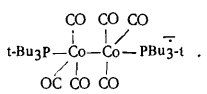
The radical-anions produced are relatively stable and the g-factors are 1.9800–2.0210. The unpaired electron interacts with the substituent Y (a_H = 10 G, a_F = 10.8 G) and also with the three equivalent ^{59}Co nuclei (I = 7/2), which leads to the appearance of 22 lines in the EPR spectrum with the constants $a_{^{59}Co}$ = 34.2–37.1 G.

The preparation of dinuclear cobalt radical-anions has been described[83]:



$$R = H, COOMe, Si(Me)_3, Si(Ph)_2Me, CH_2COOMe .$$

Complexes of another type with tri(t-butyl)phosphine ligands have the following structure[84]:



It has been suggested[84] that the unpaired electron occupies the Co–Co σ^* orbital, involving at the same time the P–Co–Co–P chain of atoms. The uniform distribution of the unpaired electron density over the two Co atoms makes it possible to treat such a dinuclear paramagnetic complex either as a compound with "mixed" valence metal species $Co^0 - Co^+$ or as formally a compound of +0.5-valent cobalt[83]. In all probability both these hypotheses are arbitrary and are most probably concerned merely with terminology. Evidently the immediate ligand environment also participates in the distribution of spin density[85]:

$$[X_2Co_2(CO)_6]^{\cdot-}$$
$$X = H_2C_2, t\text{-}Bu_2C_2, Ph_2C_2, MeC_2SiMe_3,$$
$$PhC_2SiMe_3, CF_3C_2SiMe_3, (CF_3)_2C_2, P_2, As_2;$$
$$a_{^{59}Co} = 2.37\text{–}2.88 \text{ G}, \quad a_P = 3.74 \text{ G}, \quad a_{As} = 2.12 \text{ G}.$$

One of the common methods of generating free radicals is homolytic bond dissociation. This method is suitable for the preparation of paramagnetic products on ultraviolet irradiation of dinuclear complexes of transition metals[86]. The photolysis of bis(tributylphosphine)dimanganese octacarbonyl $Mn_2(CO)_8(PBu_3)_2$ (the reaction is carried out in the presence of an excess of tributylphosphine) or tris(triethoxyphosphino)dimanganese heptacarbonyl $Mn_2(CO)_7[P(OEt)_3]_3$ in heptane with periodic removal of the CO evolved leads to the formation of paramagnetic intermediates. The EPR spectrum of the frozen irradiated solution indicates the presence in the system of the radical $Mn(CO)_3(PBu_3)_2^{\cdot}$ (its structure consists of a tetragonal pyramid with *trans*-axial phosphine ligands). The radical formed reacts slowly with the solvent, the reaction involving the abstraction of a hydrogen atom, which is typical for active free radicals. The formation of all possible products as a result of the free-radical reactions can be represented schematically as follows:

$$Mn_2(CO)_8L_2 \overset{h\nu}{\rightleftharpoons} 2Mn(CO)_4L^{\cdot} ;$$
$$Mn(CO)_4L^{\cdot} + L \rightleftharpoons Mn(CO)_3L_2^{\cdot} + CO ;$$
$$Mn(CO)_3L_2^{\cdot} + Mn(CO)_4L \rightleftharpoons Mn_2(CO)_7L_3 ;$$
$$2Mn(CO)_3L_2^{\cdot} \overset{h\nu}{\rightleftharpoons} Mn_2(CO)_6L_4 ;$$
$$Mn(CO)_3L_2^{\cdot} + HR \overset{h\nu}{\rightleftharpoons} HMn(CO)_3L_2 + R^{\cdot} .$$

The EPR spectrum has a hyperfine structure with two equivalent ^{31}P nuclei (I = 1/2, $a_{\parallel}$ = 20 G, $a_{\perp}$ = 19 G) and with one ^{55}Mn nucleus (I = 5/2, $a_{\parallel}$ = 54.1 G, $a_{\perp}$ = 35.7 G); the g-factor is 2.040. A similar situation is observed also for triethyl phosphite derivatives of manganese[86].

Apart from the photolytic method of bond dissociation with formation of free-radical species, thermolysis is also employed[87]. Thermal decomposition of manganese complexes leads, like photolysis, to paramagnetic products, whose formation can be demonstrated by the spin trapping method using t-butyl nitroxide as the trapping agent:

$$L_nM\text{—}ML_n \rightleftharpoons 2^{\cdot}ML_n; \quad {}^{\cdot}ML_n + R\text{—}N{=}O \rightarrow R\text{—}\underset{\underset{O}{|}}{N}\text{—}ML_n$$
$$R\text{—}\underset{\underset{O}{|}}{N}\text{—}ML_n \rightarrow \text{decomposition products;}$$
$$M = Mn, \ R = t\text{-}Bu, \qquad L = PPh_3, CO, PX_3, X = OMe, Et, Me, m\text{-}, p\text{-}MeC_6H_4, OEt .$$

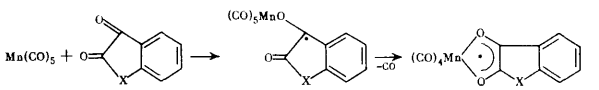
It is sometimes possible to detect the intermediate free radical, as, for example, in the case of triphenylphosphine-manganese tetracarbonyl:

$$Mn_2(CO)_8(PPh_3)_2 \rightleftharpoons 2^{\cdot}Mn(CO)_4(PPh_3)$$
$${}^{\cdot}Mn(CO)_4(PPh_3) + ON\text{—}Bu\text{-}t \rightarrow (PPh_3)(CO)_4Mn\text{—}\underset{\underset{O}{|}}{N}\text{—}Bu\text{-}t.$$

Lines due to the hyperfine interaction with the ^{55}Mn, ^{31}P, and ^{14}N nuclei are recorded in the EPR spectra. Metal carbonyls of the type $M_2(CO)_{10}$, where M = Mn or Re, have been considered in some cases[88].

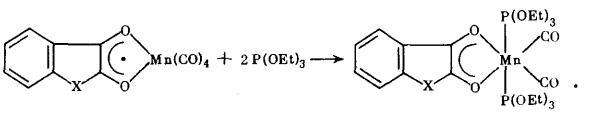
The irradiation of metal decacarbonyls in the presence of 1,2-dicarbonyl compounds[89] results in the formation of products of the addition of free radicals to diketones:

$$Mn_2(CO)_{10} \rightleftharpoons 2^{\cdot}Mn(CO)_5 ;$$

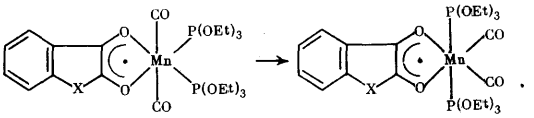


$$X = CO, NH, O, S .$$

The interaction of the resulting paramagnetic chelate with phosphines yields products of further reactions, but the paramagnetism of the molecule is maintained, an additional hyperfine interaction with the ^{31}P nuclei of the triethylphosphine ligands being observed:

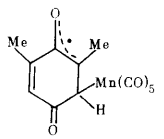


The authors[89] suggest that *cis–trans* isomerisation takes place in paramagnetic complexes of this type:

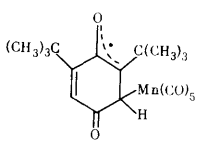


Chelates of the above type will be described below. The interaction with quinones and α-diketones of free metal-centred radicals, formed as a result of the thermal or

photolytic cleavage of the metal–metal bond in $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $(Me)_3SnMn(CO)_5$, and $Me_2Sn[Mn(CO)_5]_2$ has been thoroughly investigated by EPR.[90] Dimethylbenzoquinone, phenanthrenequinone, etc. have been used as the trapping agents. The differences between the structures of the quinones employed have a significant influence on the nature of the paramagnetic products formed. When *para*-quinones are used, the compounds formed can be regarded as organometallic σ-radicals with a paramagnetic fragment of the allyl type in the ligand:



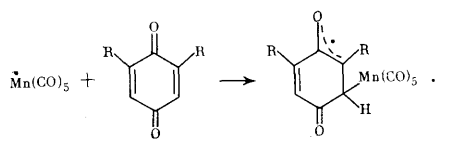
$a_H(Me) = 5.52$ G
$a_H(Mn) = 1.51$ G



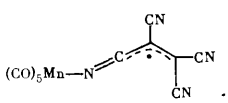
$a_H(Mn) = 3.38$ G .

The following scheme for the formation of these paramagnetic species has been proposed[90]:

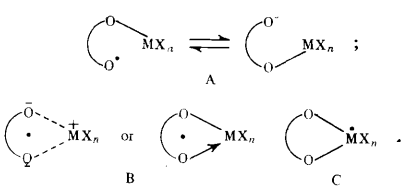
$$Q + (CO)_5MnMn(CO)_5 \underset{\text{or } \Delta}{\overset{h\nu}{\rightleftharpoons}} \left[Q^{\cdot-}(CO)_5\overset{+}{\dot{M}}n\dot{M}n(CO)_5\right] \xrightarrow{-Q^{\cdot-}} (CO)_5\overset{+}{\dot{M}}n\dot{M}n(CO)_5 \longrightarrow \dot{M}n(CO)_5 + \overset{+}{\dot{M}}n(CO)_5 \ ;$$



An analogous mechanism describes the reaction of $Mn_2(CO)_{10}$ with tetracyanoethylene, which results in the formation of an iminotricyanoallyl radical[91]:



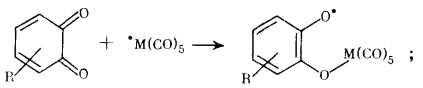
When the metal carbonyl dimers interact with *ortho*-quinones, it is necessary to consider in this instance several probable structures of the products formed[92]: structures of the phenoxy-type with localisation of the organometallic fragment at one of the oxygen atoms (A), a structure of the semi-quinone or chelate type (B), and a metal-centred radical (C):



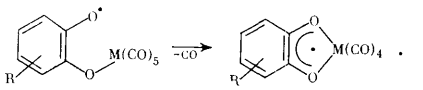
The addition of the fragment $^{\cdot}M(CO)_5$, formed on dissociation of the initial dimer, leads to structure (A), which is stable only at a low temperature. Slight heating results in the elimination of one CO group and the EPR spectra indicate the formation of structure (B), characterised by a symmetrical distribution of the spin density and a hexacoordinate manganese atom. The free radicals corresponding to structure (B) have been postulated for a series of quinones[93].

Overall, the reaction of dinuclear metal carbonyls with *ortho*-quinones can be represented by the following chain of transformations:

$$(CO)_5MM(CO)_5 \longrightarrow 2^{\cdot}M(CO)_5 \ ; \qquad (1)$$



(2)



(3)

The activation energy for the unimolecular reaction (3) (17.3 kcal mol^{-1}) and the rate constant ($k_{-20^\circ} = 0.07$ s^{-1}) as well as all the spectroscopic characteristics of the primary [reaction (2)] and secondary [reaction (3)] radicals have been published[92].

If homolysis does not precede the formation of the reaction products, it is possible to postulate a reaction pathway[94] where the interaction of $M_2(CO)_{10}$ with the acceptor A takes place in the first stage via one-electron transfer and is followed by a rearrangement in a cage:

$$(CO)_5MnMn(CO)_5 + A \xrightarrow{h\nu \text{ or } \Delta} [(CO)_5MnMn(CO)_5^{+} A^{\cdot-}] \xrightarrow{\text{fast}} \rightarrow [(CO)_5Mn^{\cdot}(CO)_5Mn{-}A^{\cdot}] \rightarrow (CO)_5Mn^{\cdot} + (CO)_5Mn{-}A^{\cdot} \ .$$

In the study of oxidation-reduction processes in organometallic chemistry, the problem arises of the formation of intermediate paramagnetic products and their subsequent reactions. A mechanism has been proposed[95] for electron transfer in the reactions of organoplatinum compounds having a Pt–C σ-bond with one-electron acceptors (hexachloroiridate and tetracyanoquinodimethane TCNQ):

$$R_2PtL_2^{+} \left\{ \begin{array}{l} \xrightarrow{\text{fast}} RPtL_2^{+} + R^{\cdot} \xrightarrow[-IrCl_5^{3-}]{IrCl_6^{2-}} RCl \ ; \\ \xrightarrow[-IrCl_5^{3-}]{IrCl_6^{2-}} R_2PtL_2Cl^{+} \ ; \end{array} \right.$$

$R = Me, Et$; $L = PPh_3$, PMe_2Ph .

The ease of one-electron oxidation decreases in the sequence $Et_2Pt(PMe_2Ph)_2 > Me_2Pt(PMe_2Ph)_2 > Et_2Pt(PPh_3)_2 > Me_2 . Pt(PPh_3)_2$.

The oxidation of R_2PtL_2 by TCNQ results in the formation of a radical pair; the TCNQ radical-anion is manifested in EPR spectra. Further reactions follow after the emergence of the radicals from the cage. Overall, the picture is identical with that in the decomposition of organometallic compounds of non-transition metals (Mg, Hg, Sn, Pb):[96]

$$R{-}MX \xrightarrow{-e} [R{-}MX]^{+} \rightarrow R^{\cdot} + MX^{+} \ .$$

A characteristic feature of transition metal complexes is their ability to undergo a change in coordination number after a change in the state of oxidation. For this reason, there is a possibility also of another pathway involving transformation into quadrivalent platinum compounds; the two possibilities are approximately equivalent for *cis*-dimethylbis(triphenylphosphine)platinum:

$$cis\text{-}Me_2Pt(PPh_3)_2 \xrightarrow[MeCN]{} \left\{ \begin{array}{l} \xrightarrow{54\%} (Me)Pt(PPh_3)_2X_2 \ ; \\ \xrightarrow{46\%} (Me)Pt(PPh_3)_2X + MeCl \ ; \end{array} \right.$$

$X = Cl, IrCl_5(MeCN), MeCN$.

In contrast to the preceding example, dialkyl(bipyridyl)-iron gives rise on oxidation with bromine to a mixture of hydrocarbons—the products of the disproportionation or

dimerisation of the radicals R$^{\cdot}$:[97]

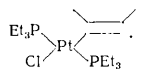
$$\left.\begin{matrix} R \\ R \end{matrix}\right\rangle Fe(bipy)_2 + Br_2 \left\{\begin{matrix} \longrightarrow R{-}R + Fe(bipy)_2 \\ \swarrow \longrightarrow 2RBr + FeBr_2(bipy)_2 \end{matrix}\right. ;$$

In this case the coordination number of iron atoms diminishes.

Aryl compounds of nickel decompose with partial coordination of a solvent molecule:

$$Ar_2NiL_2 \xrightarrow{-e} Ar_2NiL_2^{\ddagger} + S \xrightarrow{fast} Ar_2NiL_2(S)^{+} \xrightarrow{slow} \text{products}.$$

The formation of the alkenebis(triethylphosphine)platinum chloride radical has been noted[98]:



Paramagnetic palladium complexes of the π-allyl type, which exhibit a high catalytic activity, have been described as intermediates in the hydrogenation of nitro-compounds[99].

Nowadays the EPR method is widely used in the study of the paramagnetic complexes formed in catalytic processes[100]. Transition metal derivatives can behave as initiators of radical reactions of organic halogeno-compounds[101]. At any rate it is evident that many reactions in organometallic chemistry can proceed via the formation of free radicals. We shall consider some further examples.

On the basis of the study of the kinetics of the formal oxidative elimination reaction, it has been postulated that radical-cations are formed from iron complexes as an elementary stage of the reaction[102]

$$[Fe(CO)_3L_2] + I_2 \rightarrow [Fe(CO)_3L_2]^{\ddagger} + I^{\cdot} + I^{-} ;$$
$$[Fe(CO)_3L_2] + I^{\cdot} \rightarrow [Fe(CO)_3L_2]^{\ddagger} + I^{-} \text{ etc.}$$

The radical-cations formed were investigated by EPR.[102] The changes in the characteristics of the EPR spectra as a function of the electron-donating properties of the ligand L, where L = PPh_3, $AsPh_3$, $PMePh_2$, $P(NMe_2)_3$, $P(OPh)_3$, or $Ph_2PCH_2PPh_2$, have been traced. In all cases the EPR spectra indicate the occurrence of a hyperfine interaction with two equivalent nuclei of the donor heteroatom (P, As). For a full identification of the intermediate, the radical-cation was obtained by specific electrochemical synthesis:

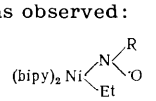
$$Fe(CO)_3L_2 \xrightarrow[\text{Pt electrode}]{-e} [Fe(CO)_3L_2]^{\ddagger} ,$$

and by interaction with a silver salt; in the presence of a halogen X the reaction proceeds with formation of a diamagnetic salt:

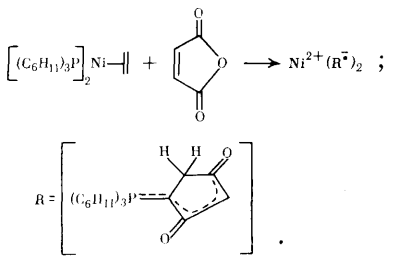
$$Fe(CO)_3L + AgPF_6 \xrightarrow{X_2} [Fe(CO)_3L_2][PF_6] .$$

The paramagnetic radical-cation $[Fe(CO)_3L_2]^{\ddagger}$ formed has the structure of a trigonal bipyramid with the *trans*-configuration.

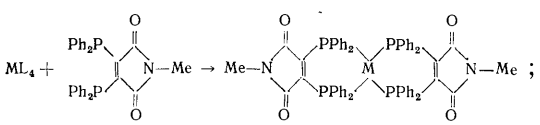
In the study of the mechanism of the aldol condensation and oxidation-reduction processes in the presence of organic σ-complexes of nickel with the aid of the spin trapping method[103], the involvement of free-radical intermediates of the following type was observed:



The interaction of ethylenebis(tricyclohexylphosphine)-nickel with maleic acid anhydride proceeds in an unexpected manner[104]. It has been suggested that intermolecular ligand exchange (the replacement of ethylene by the anhydride in the coordination sphere of the metal) results in further reactions with formation of a radical-ion salt (see below). The description of the compound obtained as a complex with a radical-anion ligand is based on spectroscopic data (EPR, ultraviolet spectroscopy). The doublet of triplets in the EPR spectrum characteristic of the given radical-anion is due to hyperfine interaction with the ^{31}P nucleus (a_P = 13.1 G) and two protons (a_H = 2.04 G). In the visible region the spectrum contains a band characteristic of the nickel(II) cation[104].



Radical complexes with maleic acid derivatives have been obtained also for palladium and platinum[105]. The interaction of zerovalent palladium, platinum, and nickel complexes with diphosphine derivatives of maleic anhydride leads to a diamagnetic complex of the zerovalent metal, stable in air, only in the case of nickel:



L=PPh_3, M=Pd, Pt; L=CO, M=Ni .

The palladium and platinum complexes are paramagnetic products unstable in air. It may be assumed that the ligand becomes a radical-anion as a result of electron transfer from the metal:

$$M^0(PP)_2 \rightarrow M^I[(PP)_2]^{\overline{\cdot}} .$$

Signals due to the hyperfine interaction with the two ^{31}P and N nuclei and the hydrogen atoms of the methyl group [a_P = 9.6 G, a_N = 3.0 G, and $a_{H(Me)}$ = 0.68 G] have been recorded in the EPR spectra. The HFI constants obtained are close to those for the paramagnetic salt $PP^{\overline{\cdot}}K^{+}$.

The photolytic interaction of cobalt complexes with sulphonyl chloride proceeds as the addition of the active free radical to the double bond, giving rise to paramagnetism in the ligand sphere of cobalt[106]:

$$RSO_2^{\cdot} + [R'R''C{=}CHCH_2CoL_2Py] \rightarrow$$
$$\rightarrow [RSO_2CR'R''CHCH_2CoL_2Py] \left\{\begin{matrix} \rightarrow RSO_2CR'R''CH{=}CH_2 \\ \rightarrow [Co^{II}L_2Py] \end{matrix}\right. .$$

An interesting example of the homolytic cleavage of the metal–ligand bond is the anaerobic photolysis of derivatives of cobaltoxime via the mechanism[107]

$$Co^{III}\text{—}R \xrightarrow{h\nu} Co^{II} .$$

In the presence of oxygen a peroxide is formed in this reaction[108]:

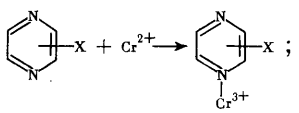
$$Co^{III}\text{—}R \xrightarrow{h\nu} Co^{II}R^{\cdot} \xrightarrow{O_2} Co^{III}\text{—}O\text{—}O\text{—}R .$$

Paramagnetic organometallic compounds can also be formed as a result of interaction with an organic free radical[109]:

$$Ag + {}^{\cdot}CH_2CN \rightarrow Ag^{\overline{\cdot}}CH_2CN ;$$
$$Ag + {}^{\cdot}CH_2OH \rightarrow Ag^{\overline{\cdot}}CH_2OH ;$$
$$Ag^{+} + CH_3CN^{\overline{\cdot}} \rightarrow Ag\text{—}C(CH_3){=}N^{\cdot} .$$

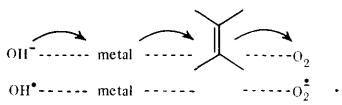
There is also a possibility of the reduction of a ligand to a

paramagnetic species with its simultaneous coordination to the reductant metal[110]:



X = Me, Cl, COOH, $CONH_2$.

An extremely interesting study[111] of metal-catalysed photochemical organic reactions of olefins involved simultaneously several important problems. A chain mechanism of the intramolecular electron transfer was postulated. The donor is the hydroxide ion and the final acceptor is oxygen:



Electron transfer proceeds via a chain with participation of a transition metal atom (Fe). The development of studies of this type can apparently elucidate the mechanisms of enzymatic oxidation reactions.

Thus a fairly large number of paramagnetic complexes are known whose magnetic properties are determined either by the electronic configuration of the central ion or by the appearance of an unpaired electron as a result of an oxidation-reduction process. An odd number of electrons in the *d* and *f* levels of the central ion in the first group of compounds does not cause qualitative changes in the nature of the metal–ligand bond and the structure of the complex and in essence such compounds differ little from their diamagnetic analogues. As regards charged paramagnetic compounds, it is rarely possible to obtain stable radicals; all the measurements are made at low temperatures and it is rarely possible to isolate the product.

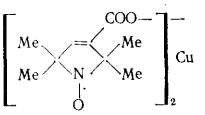
The essential requirements are, firstly, a relative simplicity of the synthesis and, secondly, the possibility of the preparative isolation of stable paramagnetic compounds. The development of the chemistry of free radicals made it possible to satisfy these requirements, which permitted the employment of stable organic radicals as ligands. Mainly stable nitroxy- and *ortho*-semiquinone paramagnetic ligands are used nowadays in the chemistry of transition metal complexes. In addition, a large number of examples of variable-valence metal complexes with nitric oxide[112] or its derivatives, coordinated via the N–O bond, have been described in the literature[113–124].

IV. STABLE NITROXY-RADICALS IN TRANSITION METAL COMPLEXES

The class of nitroxy-radicals is of considerable interest in view of their high stability[125]. These radicals have found extensive applications as spin labels and paramagnetic probes for the study of molecular dynamics and the structures of liquids in polymeric formations, biological systems, etc.[126].

Nitroxy-radicals are π-electron radicals. In aliphatic nitroxy-radicals the unpaired electron is localised almost wholly in the N–O fragment; after the introduction of aromatic substituents (R^1, R^2 = Ar), the spin density on the N and O atoms diminishes owing to the establishment of a conjugation system and a considerable proportion of the unpaired electron density is transferred to the aromatic rings[127,128].

The synthesis of the copper salt of 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-yloxy-radical was described for the first time in 1966:[129]



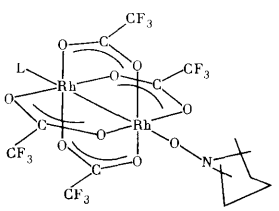
This compound was isolated in the form of a stable crystalline substance. In the solid state the salt does not give rise to an EPR signal, while in solution (in water and ethanol) a weak signal can be recorded.

Thus it became possible to synthesise from derivatives of nitroxy-radicals complexes with ligands known to be paramagnetic beforehand. Nitroxy-radicals are, in principle, ambifunctional ligands and the complexes based on them can be divided into two classes in accordance with the type of ligand–metal coordination:

(1) Coordination via the N–O group carrying the unpaired electron; this leads to a spin–spin interaction between the nitroxy-fragment and the metal ion, provided that its isotope is paramagnetic.

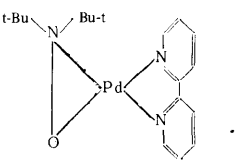
(2) Coordination via other functional groups of the ligand which show a greater tendency towards complex formation than the N–O group; there is then a possibility of exchange interactions of the radical centres with one another and with the metal ion.

The first case is of no particular interest because in compounds of this kind there is a possibility of the disappearance of paramagnetism; however, for example, in the EPR spectrum of the product of the addition of the nitroxy-radical to the rhodium trifluoroacetate dimer[130], the signal is split owing to the interaction with the ^{103}Rh nucleus ($I = 1/2$, $a_{Rh} = 1.7$ G).



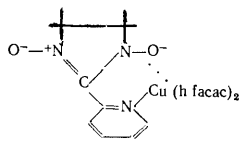
In this case the unpaired σ-electron is donated by the nitroxy-group to the d_{z^2} orbital of rhodium and there is a reverse interaction of the d_{xy} orbital of the rhodium atom with the π* orbital of the NO group carrying the unpaired electron.

An unusual three-membered ring is formed in the complex of palladium with the di-t-butylnitroxy-radical[131]:



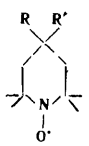
Complexes of other variable-valence metals have also been described[131–135]. It is difficult to draw a sharp boundary between compounds of the first and second types. There is a possibility of instances of coordination via a functional group accompanied by the simultaneous interaction of the metal ion with the nitroxy-fragment, which is in many respects determined by the structure of the complex. It has been shown[136–139] that the geometry of the complex influences the nature of the bond. In the series of compounds of copper, manganese, and vanadium with α-, β-,

and γ-pyridylnitronyl nitroxide, copper or vanadyl α-pyridyl-nitronylnitroxide bishexafluoroacetylacetonate is diamagnetic:



The occurrence of additional coordination of this type can be accounted for by intermolecular electron transfer from the $d_{x^2-y^2}$ orbital of copper or the d_{xy} orbital of vanadium to the $2p\pi$ orbital of the nitroxy-group and is based on the energies of the singlet–triplet cleavage.

Table 1. Transition metal complexes of the type ML_nX_m containing the iminoxy-fragments

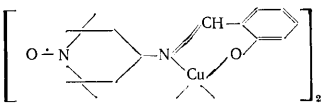


R, R'	ML_nHal_m	References
R=R'=H	CoL_2I_2	[141]
»	$(PdLCl)_2$	[141]
»	$CuLCl_2$	[141]
»	$[Rh(hfacac)_2]L$	[130]
R=H, R'=NH_2	CoL_2I_2	[141]
»	PdL_2Cl_2	[141]
»	CuL_2Cl_2	[141]
»	NiL_2Hal_2	[142]
»	PtL_2Hal_2	[142]
»	ZnL_2Hal_2	[142]
R=NH_2, R'=COOH	CoL_2	[141]
»	$NiL_2\cdot 2H_2O$	[141]
»	PdL_2	[141]
»	$PtL_2\cdot 2H_2O$	[141]
»	CuL_2	[141]
»	ZnL_2	[141]
R=H, R'=COOH	ML_2, where M=Cu, Co, Pd, Pt, Zn, Ni	[142]
R=H, R'=—N=CH—CH=N—	$PdLCl_2$	[141]
»	$(CuLCl)_2$	[141]
R=H, R'=—N=CH—C_6H_4—O—	CuL_2	[143, 145]
»	FeL_3	[143, 145]
»	CoL_2	[143, 145]
»	NiL_2	[143, 145]
»	ZnL_2	[143, 145]
R=H, R'=O—C(=S)—S—	ZnL_2	[146]
»	HgL_2	[146]
»	CoL_2	[146]
»	NiL_2	[146]
R, R'=N—N=C—NH_2 (S)	CoL_2	[144]
»	NiL_2	[144]
»	CuL_2	[144]
»	ZnL_2	[144]
R=H, R'=—N=C—(C=N→)	$CuL(hfaa)_2$	[147], 148]
R=H, R'=—NH—C(=O)—R*	CuL	[151]
R=Ph, R'=H	$[PdLX]_2$	[151]

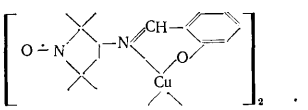
*R_p = porphyrin residue.

In the zinc compounds with a similar mode of coordination there is no direct interaction with the radical centre[140]. There are more numerous examples of transition metal complexes with coordination via the functional groups of the substituents in the radical ligands. In the main these are derivatives of 2,2,5,5-tetramethylpiperidin-1-yloxy-, 2,2,5,5-tetramethyl-Δ^3-imidazolin-1-yloxy-, and 2,2,5,5-tetramethylpyrrolin-1-yloxy-radicals. The types of complexes based on the piperidinyloxy-radical are presented in Table 1.

The magnetic properties of complexes with paramagnetic ligands have been investigated by determining the magnetic susceptibilities and by EPR.[149,150]. The magnetic susceptibility of the copper complex of the Schiff base[152]

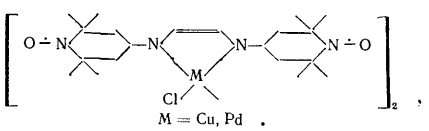


indicates the presence of three unpaired electrons in the molecule and is equal to the sum of the susceptibilities of three non-interacting or weakly interacting spins. However, the analogous complex differing by only one methylene unit in the ring of the radical proved to be diamagnetic in the crystalline state, which the authors explain by the formation of the coordinate bond $NO^{\cdot} \rightarrow Cu^{2+}$ in the polymeric crystal lattice:



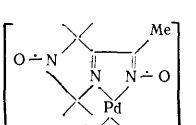
The EPR spectra of the solutions indicate the occurrence of weak exchange interactions in the radical centres and Cu^{2+} ions.

The nickel(II), palladium(II), and zinc(II) complexes of the 4-amino-4-carboxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical give rise to triplet spectra typical for nitroxy-radicals[141], which do not differ significantly from the spectra of the free radicals. A change of temperature also does not affect the nature of the spectra. For the palladium(II) and copper(II) complexes of the biradical ligand



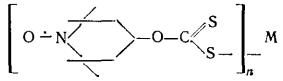
M = Cu, Pd .

an EPR spectrum characteristic of free radicals with a weak exchange interaction between the radical centres was obtained: $I < a$, where a = 15 G is the constant for the hyperfine interaction of the unpaired electron in the ^{14}N nucleus and I the exchange interaction energy. The exchange interactions in dimeric complexes are manifested spectroscopically by additional lines in the EPR spectrum relative to the initial ligand. These data make it possible to confirm the structure of the dimeric complex with the aid of a spin label[153]:



For the cobalt(II) and palladium(II) complexes of the 4-amino-2,2,6,6-tetramethylpiperidin-1-yloxy-radical, it is possible to observe in the EPR spectrum a quintet corresponding to strong exchange between the radical centres, i.e. $I \gg a$. In the analogous copper(II) complex the unpaired electron of the radical ligand interacts with the copper ion, to which corresponds a broad signal in the EPR spectrum[154].

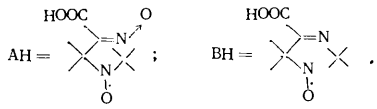
For the complexes with the paramagnetic xanthate ligands[146]



M = Zn (II), Hg (II), Co (III), Ni (II) ,

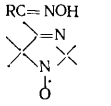
the g-factors are in the range 2.0075–2.0089, which differs little from the g-factors of the nitroxy-radicals. This can be explained by the fact that in the given complexes the metal ions interact only weakly with the radical centres. At room temperature the EPR spectra of the solutions are characterised by a triplet (a_N = 15–16 G). A weak intramolecular spin exchange between two radical centres is exhibited for zinc and mercury (the intensity of the biradical components is ~5% of the main signal).

Transition metal acetates containing paramagnetic fragments of the following type have been obtained[155]: $CoA_2.2H_2O$, $NiA_2.2H_2O$, $CuA_2.2H_2O$, $ZnA_2.2H_2O$, $PrA_3.3H_2O$, $EuA_3.2H_2O$, $CoB_2.4H_2O$, $CuB_2.4H_2O$, $ZnB_2.4H_2O$, and PdB_2.



A single broad line with a g-factor equal to the mean of the g-factors of the metal ion and the ligands is observed in the EPR spectra of the copper(II) complexes. In the copper(II) and nickel(II) compounds there is an exchange interaction between the paramagnetic centres; the zinc(II) and palladium(II) complexes give rise to quintets typical for biradicals; in praseodymium(III) and europium(III) acetates there is no exchange interaction between the paramagnetic centres, i.e. the usual triplet is observed in the EPR spectrum (a_N = 15.1 G).[156,157]

The 4-hydroxyiminomethyl-2,2,5,5-tetramethyl-Δ^3-imidazolin-1-yloxy-radical forms chelate rings with the copper(II), nickel(II), palladium(II), cobalt(III), and zinc(II) ions via the oxime group and the electron-donating ring nitrogen atom:



R = H, Me .

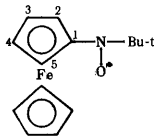
A quintet typical for biradicals has been recorded in the EPR spectra of such complexes[158,159].

The EPR spectra of solutions of the analogous copper(II), nickel(II), cobalt(III), and palladium(II) (R = Me) complexes[160] in chloroform have not been observed, which is a consequence of the strong exchange interaction between the metal ions and the paramagnetic ligands, which leads to a marked decrease of the electronic relaxation time. The EPR spectra of the cobalt(III) and palladium(II) chelates are quintets.

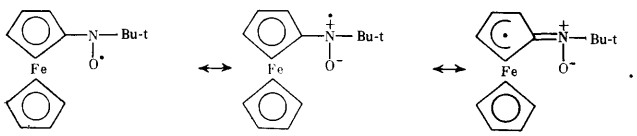
All the examples enumerated above permit the conclusion that there is only a weak interaction between the radical centre and the metal ion in complexes of the above type or that such interaction is altogether absent, which implies that the paramagnetic ligand hardly introduces any changes into the usual complexes, be they acetates, xanthates, or Schiff bases, and functions only as a paramagnetic label. This is due to the absence of a conjugation chain between the radical centre and the metal.

A completely different picture is observed in complexes in which the metal atom is involved in a conjugation chain with the paramagnetic fragment. Unfortunately such examples are extremely rare. However, it is clear that in cases of this kind the unpaired electron interacts with the orbitals of the metal atom.

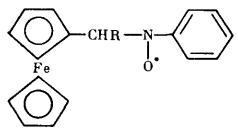
In the stable nitroxyferrocenyl radical[161]



the spin density at the ^{14}N atom is smaller than in the di-t-butylnitroxy-radical ($a_{^{14}N}$ = 13.3 G) and the g-factor (2.0149 ± 0.0004) exceeds the g-factor for arylnitroxy-radicals (2.006). The HFI constant (0.8 G) corresponding to the second and fifth ring protons is smaller by a factor of 2.5 than the HFI constant for the remaining protons ($a_{O-H} \cong$ 2.0 G) in the aryl fragment of the phenyl-t-butyl-nitroxy-radical (PTN). The following mesomeric structures have been proposed[161] taking into account conjugation:



The constants a_N = 10.9 G and a_H = 2.95 G have been obtained for the nitroxy-radical separated from the ferrocenyl substituent by a carbon atom[162]:

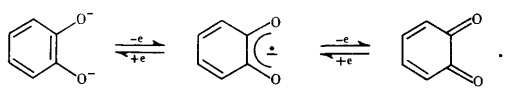


R = MeC_6H_4, Ph, Me .

V. TRANSITION METAL COMPLEXES WITH *ORTHO*-SEMIQUINONE LIGANDS

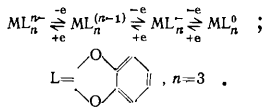
There has always been an extremely great interest in aromatic dicarbonyl compounds, starting with the first studies by Michaelis[163,164], who postulated the formation from quinones in biochemical reactions of the active forms of certain enzymes as radical species. Sufficient data concerning the role of quinone derivatives in oxidation-reduction enzymatic processes have now accumulated[165].

Compounds of the type of *ortho*-quinones[166] are characterised by the formation of the redox triad:

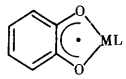


dianion *ortho*-benzosemiquinone *ortho*-benzoquinone

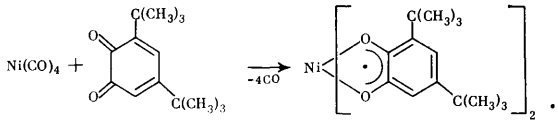
It was to be expected that a similar system, linked by one-electron transitions, is formed also by transition metal chelates:



In this series a complex is formed with the unpaired electron in the ligand:



The synthesis of a nickel complex by the reaction of nickel tetracarbonyl with 3,5-di-t-butyl-1,2-benzoquinone was reported in 1966:[167]

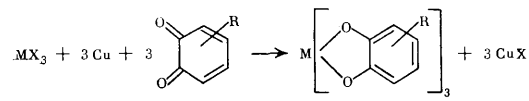


Chromium, molybdenum, and tungsten complexes based on *o*-chloranil were obtained in 1974.[168–171]

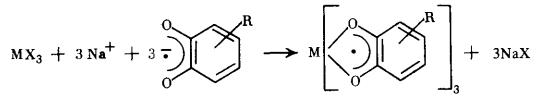
The chemistry of transition metal complexes with paramagnetic *ortho*-semiquinone ligands was developed to the greatest extent in the studies by Razuvaev, Abakumov, and coworkers[172–177]. Copper, silver, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, iron, gallium, gadolinium, palladium, and nickel complexes with *ortho*-quinone fragments were obtained[173–177].

The methods of synthesis of complexes of tervalent metals can be combined in the following groups.

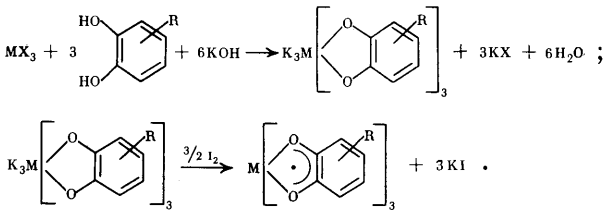
1. The interaction of metal halides and *ortho*-quinones in the presence of metallic copper:



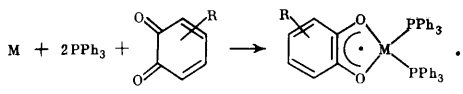
2. The reaction of transition metal halides with sodium or thallium *ortho*-semiquinolates:



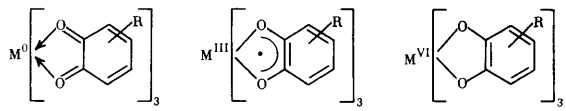
3. The exchange reaction between a transition metal salt and the catechol dianion:



4. The monoligand copper and silver complexes can be obtained by the direct interaction of the quinone and the metal in the presence of a stabilised ligand, for example, triphenylphosphine[176]:



Complexes of different transition metals have been synthesised in this way. Of the three possible types of structures of the above complexes, structure B is believed to be closest to reality[176]:



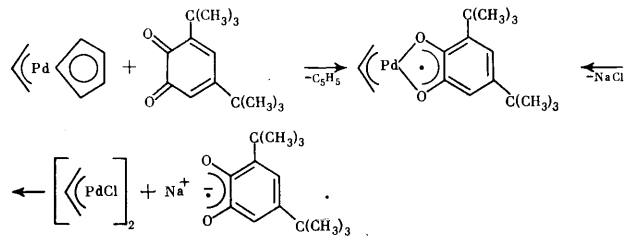
A-(quinone) B-(semiquinone) C-(catecholate)

M = Cr, Mo, W .

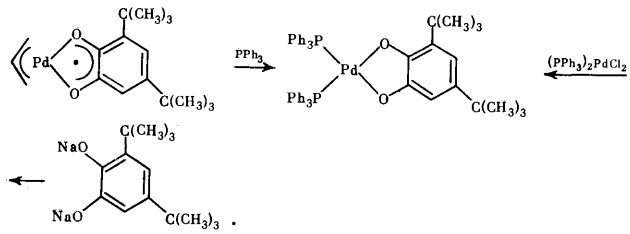
The term "quasi-radical ligands" has been proposed for the ligands of this type, implying the possibility of exchange interactions between the paramagnetic fragment and the metal ion[176].

In the general case the distribution of spin density in the paramagnetic complex does not differ significantly from that in the *ortho*-semiquinone radical-anion. In the presence of stabilising ligands ER_3 (where E = P or As and R = Ph, Et, or OEt) in the molecule of the complex, the unpaired electron is seen to interact not only with the magnetic isotopes of the metal ion but also with the ^{31}P and ^{75}As nuclei of the extraneous [sic] ligand (a_P = 12–20 G).[169]

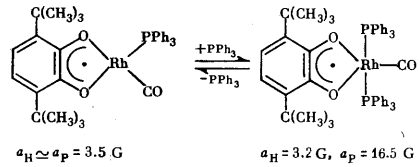
For example, the allyl group can serve as an extraneous ligand:



However, in this case it was not possible to observe the hyperfine interaction of the unpaired electron with the allyl fragment[175,176] owing to the great width of the HFS lines in the EPR spectra. The allyl complex can be converted into the corresponding triphenyl phosphine derivative:



The possibility of reversible conversion into a complex with a pentacoordinate rhodium atom (trigonal bipyramid) has been demonstrated in relation to the square-planar rhodium complex[177]:



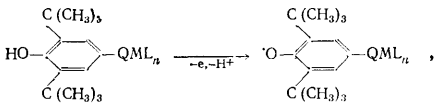
$a_H \simeq a_P$ = 3.5 G a_H = 3.2 G, a_P = 16.5 G

All the paramagnetic complexes obtained are relatively stable and they are also stable in the presence of oxygen[178,179].

Thus the data obtained demonstrate the possibility of introducing free-radical *ortho*-semiquinolate species into a molecule of the transition metal complex.

VI. PHENOXY-RADICALS IN PLATINUM METAL COMPLEXES

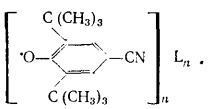
Another approach to the synthesis of paramagnetic complexes was followed when a series of stable phenoxy-radicals were used. A series of complexes based on sterically hindered phenols were obtained, their one-electron oxidation resulting in the formation of metal-containing free phenoxy-radicals[180–186]:



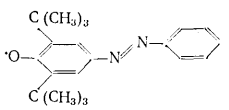
where Q is the coordinating group and M = Pd, Pt, or Ph.

The compounds obtained can be divided into several groups in terms of the type of the metal–paramagnetic ligand bond (L = Cl, Br, I, PPh_3, acac, THF, or π-C_5H_5).

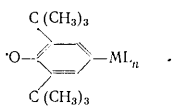
I. *n*-Donor coordination:



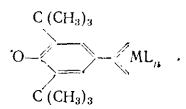
II. σ-Bond + *n*-donor coordination:



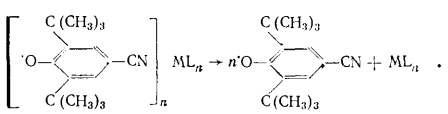
III. σ-Bond:



IV. π-Bond:



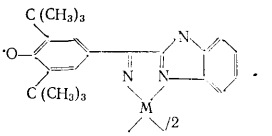
Group I free radicals are unstable and dissociate with liberation of the stable cyanophenoxy-radical into the solution:



The EPR spectra of Group II complexes are isotypical[180]; a hyperfine structure is observed, which can be explained by the interaction of the unpaired electron with the *meta*-protons of the phenoxy-ring (a_H = 1 G) and with two ^{14}N nuclei (I = 1, a = 2 G). At the same time the radical corresponding to the initial ligand is extremely unstable and decomposes rapidly even at 20 °C with liberation of molecular nitrogen, diphenoquinone, biphenyl, and their reaction products[187,188]. Its EPR spectrum is poorly resolved and yields virtually no information.

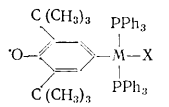
The fairly high stability of the organometallic azophenoxy-radicals in the range between −40° and +40 °C implies that the metal–carbon σ-bond, stabilised by the coordination to the nitrogen atom, is fairly stable, despite the presence of a paramagnetic fragment in the ligand, i.e. *ortho*-metallation and *n*-donor coordination (the formation of an organometallic ring) increase significantly the stability of the organic free radical. Furthermore, on formation of complexes, the spin conductivity of the azo-group increases, since in the ligand free radical the −N=N− unit is "non-conducting".

Phenoxy-radicals containing a heterocyclic fragment are also relatively stable[186]:



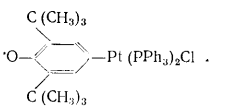
A triplet of triplets is observed in the EPR spectrum of the palladium(II) complex (a_H = 1.7 G, a_N = 4.8 G, a_{Pd} = 24 G); a septet is characteristic of the platinum(II) complex (a_H = 1.7 G, a_N = 3.4 G, a_{Pt} = 21.5 G).

The σ-bonded organometallic phenoxy-radicals obtained proved to be extremely stable[183]:



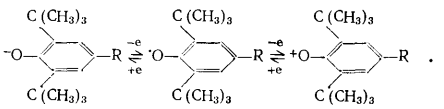
X = Cl, Br, I; M = Pd, Pt .

Their concentration does not decrease when the temperature is raised to 100 °C, they are stable for a long time in solutions, and they can be stored in evacuated bulbs for an unlimited period. A phenoxy-radical containing a platinum atom has been isolated in the solid state:



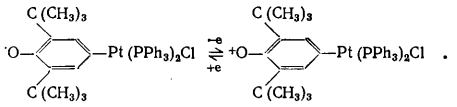
Its infrared spectrum does not contain the band corresponding to the vibrations of the OH bond and the band due to the stretching vibrations of the >C=O group appears in the region of 1640 cm^{-1}. The platinum-containing radicals are more stable than their palladium analogues. Depending on the nature of the halogen, the stability of the radicals decreases in the sequence Cl > Br > I. The unpaired electron interacts with the *meta*-protons of the phenoxy-ring, with the magnetic isotopes of the transition metal, and also with two equivalent ^{31}P nuclei (Table 2), which indicates a *trans*-geometry of the complex. The constants for the hyperfine interaction with the *meta*-protons in the palladium and platinum derivatives indicate the electropositive nature of the organometallic group. The high constant for the hyperfine interaction with the palladium and platinum nuclei and with the phosphorus nuclei of the triphenylphosphine ligands indicate a significant involvement of the *d* orbitals of the transition metal and the *p* orbitals of the phosphorus atom of triphenylphosphine in the distribution of spin density.

The free radicals exhibit a dual reactivity: in reactions with reductants they accept one electron and in reactions with oxidants they give up one electron:



The reduction of phenoxy-radicals to phenoxide ions constitutes a fairly trivial fact. Oxidation with formation of the phenoxylium cation has been described only for a limited number of organic derivatives[189,190]. In relation to stable σ-bonded derivatives, it proved possible to observe the reducing properties of organometallic radicals. The platinum-containing phenoxy-radical is oxidised by vanadyl chloride or tetracyanoquinodimethane to the phenoxylium

cation with retention of the metal–carbon bond:



Initially one observes in the EPR spectra a superposition of two spectra—that of the initial phenoxy-radical and that of the radical-anion $TCNQ^-$. After a time, the signal of the initial phenoxy-radical disappears and the spectra show only the signal due to $TCNQ^{\cdot}$. As the reductant is added, the signal of the radical-anion $TCNQ^-$ gradually disappears and the signal of the initial platinum-containing phenoxy-radical takes its place, which demonstrated the reversibility of the reaction.

Table 2. The EPR parameters of the σ-bonded derivatives of phenoxy-radicals (toluene, 25 °C).[183]

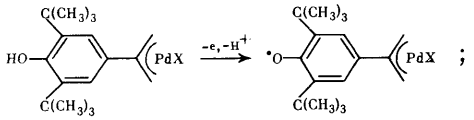
M	α*, %	I	a_H, G	a_{31P}, G	a_M, G	g-factor
Pt	33.7	1/2	1.2	16.0	94.0	2.0079
Pd	22.2	5/2	1.5	18.7	5.15	2.0051

*Natural abundance of the magnetic isotope.

Table 3. The EPR parameters of the π-allylpalladium-containing phenoxy-radicals (toluene, 25 °C).[184]

X	a_H^{meta}, G	a_H^{all}, G	a_{Pd}, G	g-factor
Cl	1.8	0.9	12.2	2.0051
Br	1.8	0.9	11.5	2.0057
I	1.8	0.9	10.3	2.0076
PPh_3Cl	1.8	0.9	9.2	2.0052
acac	1.8	0.9	—	2.0043
C_5H_5	1.6	0.8	5.4	2.0038

Phenolic π-allyl derivatives have been used to generate π-allylpalladium-containing phenoxy-radicals[184]:

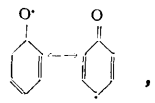


X = Cl, Br, I, PPh_3, acac, Cp .

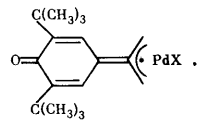
The spectroscopic parameters of the radicals obtained are presented in Table 3. The unpaired electron interacts with the *meta*-protons of the phenoxy-ring, with the protons of the terminal methylene groups of the allyl ligand, and with the magnetic palladium isotope ^{105}Pd. The last interaction results in the appearance at the edges of the main signal of satellite lines whose intensity is ~20 times lower than that of the main signal. Table 3 shows that, on passing from the chloride to the cyclopentadienyl derivative, the $a_{^{105}Pd}$ diminishes, the greatest effect being observed for the π-cyclopentadienyl ligand. In the square planar complexes this quantity diminishes monotonically with increasing bulk of the substituent at the palladium atom (Cl, Br, I, PPh_3). In the formally octahedral π-cyclopentadienyl derivative a more pronounced decrease of $a_{^{105}Pd}$ is observed. If $a_{^{105}Pd}$ is adopted as a measure of the delocalisation of the spin density, then its variation as a function of the group X will reflect the influence of the π-allylpalladium-containing group as a substituent in the *para*-position of the phenoxy-radical. The electronic characteristics of this group as a substituent in an aromatic ring are known[191].

A satisfactory linear dependence of $\delta_{^{19}F}$ and $a_{^{105}Pd}$ on the electronegativity of the ligand X ($r = 0.996$) has been observed for square planar complexes; the slope of the straight line $\rho = -7.162$ ($\Delta\rho = \pm 1.883$) indicates a greater influence of the ligands X on the distribution of spin density compared with their influence on the distribution of electron density. On passing to the formally octahedral π-allyl-π-cyclopentadienylpalladium complex[186], the linear relation is somewhat impaired ($r = 0.966$); the straight line is inclined still more steeply relative to the coordinate axis on which the values of a_{Pd} have been plotted. Thus the spin density is in some way redistributed over the metal atom in the π-cyclopentadienyl derivative, in which the electron density in the 2-position is significantly reduced as a consequence of the strong electron-donating influence of the ligand π-C_6H_5.

The parallel variation of the distributions of the electron densities in the compounds investigated is striking in both instances. As shown previously[191], the electronic effects can be transmitted between the benzene ring and the π-allyl ligand only via an inductive mechanism. The question arises whether one can assume that the transmission of spin density also involves an analogous mechanism. However, the role of the inductive effect in the distribution of electronic charge, at least in the phenoxy-part of the molecule, should be significantly smaller than the role of the conjugation effect[187–191]. It is necessary to elucidate how the charge density of the unpaired electron, delocalised to the *para*-position in the phenoxy-radical via the conjugation chain, is then redistributed to the π-allyl fragment,



and then further to the palladium atom (provided that further conjugation with the central carbon atom of the π-allyl ligand is impossible). In other words, there is no resonance structure of the type



The above question can be answered as a result of the following observation; in diamagnetic complexes the signals of the *syn*- and *anti*-protons of the π-allyl ligand are observed in the NMR spectrum for different field strengths as a consequence of the different degrees of shielding. In the EPR spectra of the corresponding free radicals a pattern is observed which indicates the equivalence of all four allyl protons (a quintet, $a_H = 1$ G). Thus the *syn-anti* exchange, leading to the equivalence of all the protons in the usual allyl complexes and observed on the NMR time scale either with increase of temperature or when the system

contains a strong electron-donating ligand, also occurs in the paramagnetic analogues under the usual conditions.

The equivalence of the four allyl protons observed on the EPR time scale following the transition from the diamagnetic to the paramagnetic system shows that the energy barrier in the intramolecular rearrangements in free radicals is lower than in the corresponding diamagnetic compounds. In other words, in paramagnetic complexes a reversible metallotropic rearrangement can take place much more readily:

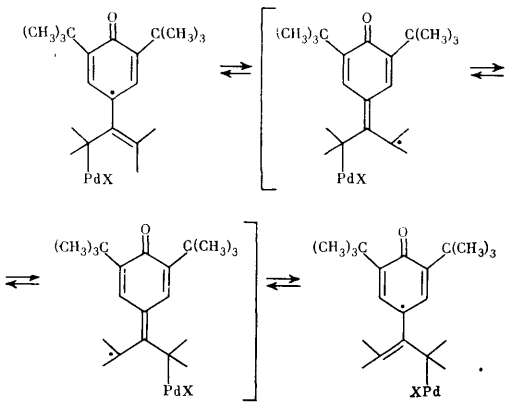


Table 4. Dependence of $a_{^{105}Pd}$ on the solvent (20 °C).[184]

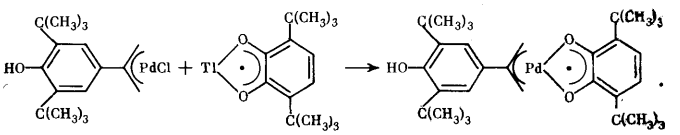
Solvent	$a_{^{105}Pd}$, G	Solvent	$a_{^{105}Pd}$, G
C_2H_5OH	14.6	Dioxan	13.2
$CH_3COC_2H_5$	13.6	Toluene	13.1

Table 5. Temperature variation of $a_{^{105}Pd}$ (toluene).[184]

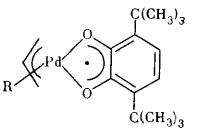
t, °C	20	0	−20	−40	−60
$a_{^{105}Pd}$, G	13.1	13.2	13.4	13.6	13.7

As a result of this, the system resembles the allyl compounds of non-transition metals, for which the decisive role of metallotropy has been demonstrated in dynamic processes, leading to the equivalence of the terminal hydrogen atoms[198].

The EPR spectra of the paramagnetic palladium complex (X = Cl) have been studied in different solvents (Table 4) and at different temperatures (Table 5). The equivalence of the four protons of the allyl ligand is maintained in all cases. Consequently the driving force of the rapid dynamic processes occurring in the paramagnetic allyl complexes is the delocalisation of the spin density over the entire molecule. The question arises whether the dynamic state of the allyl system is preserved also in the case where the paramagnetic fragment is not linked directly to the allyl ligand. A study was therefore made[184] by the EPR method of the interaction of the π-allyl complexes of palladium with thallium 3,6-di-t-butyl-*ortho*-semiquinolate:

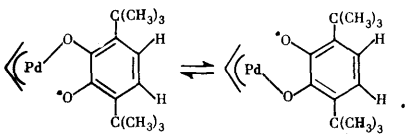


The unpaired electron interacts with two equivalent protons of the *ortho*-semiquinolate ring (a_H = 3.37 G), with the magnetic isotope ^{105}Pd (a_{Pd} = 2.35 G), and with two protons of the allyl fragment (a_H^{all} = 0.97 G). An analogous picture is observed also for other substituted π-allyl complexes.

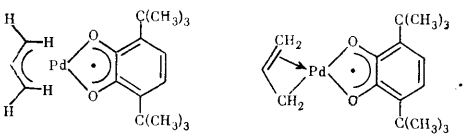


R = 2-H, 2-Ph, 2-$MeOC_6H_4$, 1-FC_6H_4 .

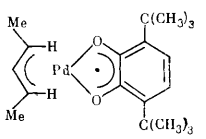
A triplet due to the two protons of the paramagnetic ligand and the two protons of the π-allyl ligand appears in all cases; each component of the triplet is split further into another triplet. The equivalence of the two protons in the *ortho*-semiquinolate ligand is a consequence of the rapid reversible migration of the palladium atom[199]:



The appearance in the EPR spectrum of the triplet due to the two equivalent protons of the π-allyl ligand can have two causes: firstly, the interaction of the unpaired electron solely with the *anti*-protons while retaining the π-allyl structure (A) and, secondly, the possibility of the freezing of the σ-structure (B):

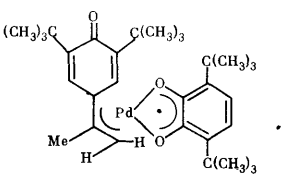


A 1,3-disubstituted allyl complex of the type



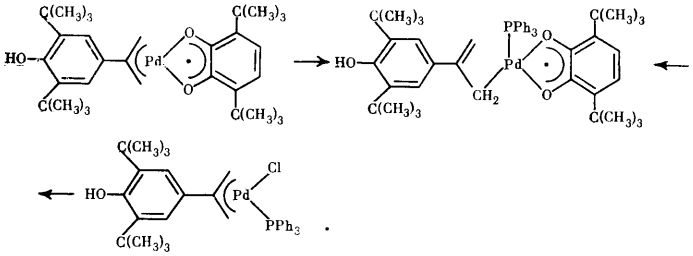
was used to solve this problem. The EPR spectrum of this radical contains a triplet caused by the interaction of the unpaired electron solely with the two *anti*-protons of the π-allyl ligand.

Analysis of the EPR spectra of an allyl complex with a quinonoid bond system leads to the same conclusion[185]:

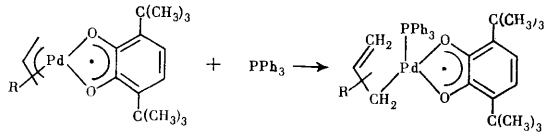


In this case the unpaired electron interacts only with one *anti*-proton of the allyl group and the HFI constant is ~0.5 G, which is smaller approximately by a factor of two than in all the cases described above[181,184].

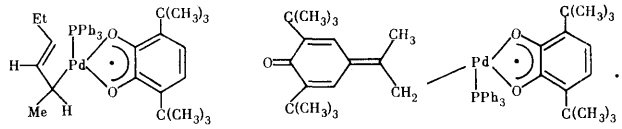
The formation of a σ-structure in the systems investigated was observed only in the presence of triphenylphosphine; the σ-complex was isolated on a preparative scale and has been obtained by specific synthesis:



An analogous transition, which led to an overall rearrangement of the bond system, has been studied spectroscopically for complexes with different substituents in the π-allyl ligand:



For R = 2-H, 2-C_6H_5, 2-$MeOC_6H_4$, or 1-FC_6H_4, a triplet due to the two protons of the terminal carbon atom is observed (a_H = 0.4–0.6 G); in addition the unpaired electron interacts with the ^{31}P nucleus ($a_{^{31}P}$ = 2.55 G). A doublet due to a single proton (a_H = 0.5 G) has been recorded in the EPR spectra of 3-ethyl-1-methylallyl-palladium *ortho*-semiquinolate, and a triplet due to two protons (a_H = 0.6 G) has been observed in the spectrum of the quinonoid complex[184]:



Thus the nature of the processes occurring in paramagnetic π-allyl complexes is determined to a significant extent by the position of the free-radical ligand relative to the allyl group. When the unpaired electron appears directly in the allyl ligand, the system becomes dynamic; on the other hand, for systems with an extraneous ligand, carrying the unpaired electron, the π character of the ligand–metal bond is retained, but the π–σ transition is significantly facilitated compared with the diamagnetic ligand corresponding to the allyl compounds.

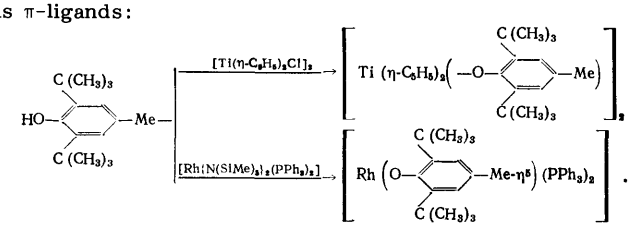
Yet another fact drew attention in the study of the free radical generated by the oxidation of π-allylpalladium-substituted phenols. The radical corresponding to the initial ligand, namely 2,6-di-t-butyl-4-isopropylphenol, is extremely unstable[200], and cannot be detected by EPR. On the other hand, π-allylpalladium-containing phenoxy-radicals proved to be fairly stable over a wide temperature range (between −50° and +50 °C). Thus coordination to the transition metal atom led to a significant stabilisation of the unstable free radical. The nature and mode of metal–ligand bonding determine to a significant extent the stability of organometallic free radicals.

The observed sequence of the influences

$$\sigma > \pi \gg n, \sigma \rangle\rangle n$$

characterises the ability of the metal atom in complexes of the above type to influence the degree of delocalisation of the unpaired electron in the molecule. In σ-phenyl compounds the unpaired electron is in essence delocalised over the entire molecule (the phenoxy-radical, the metal atom, and the phosphine ligands), which is the reason for the exceptionally high stability of the radicals formed.

Derivatives of sterically hindered phenols can function as π-ligands:



However, in this case the complexes are constructed differently and are diamagnetic derivatives of the phenoxide anion[201].

* * *

The data considered in the present review permit the conclusion that the presence of the unpaired electron in transition metal complexes permits the derivation of information about the detailed characteristics of the structures of complex and organometallic compounds as a result of the application of the EPR method in combination with other physicochemical procedures. The nature of the delocalisation of the unpaired electron in the paramagnetic coordination and organic compounds of transition metals makes it possible to infer the nature of the metal–ligand bonding and the distribution of electron density via the metal–ligand–other ligands bond system. The greatest amount of information can be deduced in the case of complexes with paramagnetic ligands under the conditions of the maximum delocalisation of the spin density of the unpaired electron over the entire molecule. Intramolecular electron transfer then takes place and the systems formed can serve as convenient models for the study of the mechanisms of the oxidation-reduction processes occurring in a living organism.

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Investigation of Paramagnetic Metallocenes and Diarene Complexes of Transition Metals by Magnetic Resonance Methods

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EPR and NMR data for paramagnetic metallocenes and diarene complexes of transition metals are presented. The analysis of the *g*-factors and the hyperfine and spin-spin interaction constants for the EPR spectra as well as the paramagnetic shifts in the NMR spectra have been used to determine the electronic configurations of the complexes. The manifestation of the Jahn-Teller effect in the EPR spectra of sandwich compounds is described. The scheme of the *d*-electronic levels in metallocenes and the mechanism of the spin delocalisation are discussed.
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I. INTRODUCTION

The nature of the bond in metallocenes and diarene complexes of metals has continuously attracted the attention of both experimenters and theoreticians. Since 1951, the time of the first synthesis of ferrocene, numerous theoretical studies, which explained the stability and aromaticity of ferrocene, have been carried out. Quantitative comparison of the theoretical results with spectroscopic data serves as an objective test of the reliability of the continuingly improving computational methods.

This review is devoted to the results of the study of paramagnetic sandwich complexes of transition metals. Examination of paramagnetic complexes alone simplifies somewhat the analysis of the electronic structure, since the EPR and NMR parameters are in this case determined by the distribution of one or several unpaired electrons and not all the electrons of the molecule.

Jaffé[1] was the first to point out the unusual nature of the chemical bond in metallocenes, consisting in the fact that this many-electron bond is formed by the molecular π orbitals of the cyclopentadienyl rings and the orbitals of the central metal ion. A quantitative theory of the chemical bond in sandwich compounds was subsequently developed by a group of workers[2-6]. A survey of the early theories can be found in a monograph[7]. These theories are based on the consideration of the symmetry of the molecular orbitals of the ligand and the orbitals of the metal. The molecular orbitals of each cyclopentadienyl ring are formed by five atomic $2p_z$ orbitals, which can be divided into three groups differing in their symmetry relative to rotation about an axis perpendicular to the plane of the five-membered ring and passing through its centre. In order of increasing energy, the above orbitals are designated by a_1, e_1, and e_2, the symbols being related to the symmetry properties. The single a_1 orbital has no nodal planes perpendicular to the plane of the ring, while e_1 and e_2 are degenerate orbitals which do have nodal planes—one in e_1 and two in e_2. Linear combinations of these localised molecular orbitals give rise to the set of molecular orbitals a_{1g}, a_{2u}, e_{1g}, e_{1u}, e_{2g}, and e_{2u} embracing both cyclopentadienyl rings. The orbitals belong to the symmetry point group D_{5d} to which ferrocene and other metallocenes having the structure of a pentagonal antiprism belong. As before, the symbols *e* and *a* refer to the degenerate and non-degenerate states. The subscripts 1 and 2 define the number of nodal planes in the *e*-type orbitals. The additional subscripts *g* and *u* indicate the symmetry properties of the new orbitals as regards inversion relative to the centre of the molecule, i.e. relative to the metal atom. Such transformation either leaves the sign of the orbital unchanged (*g*) or alters it (*u*).

The metal orbitals 3d, 4s, and 4p can also be classified as belonging to the symmetry point group D_{5d} with the aid of the representations $a_{1g}(3d_{z^2})$, $a_{1g}(4s)$, $a_{2u}(4p_z)$, $e_{1g}(3d_{xz}, 3d_{yz})$, $e_{2g}(3d_{xy}, 3d_{x^2y^2})$, and $e_{1u}(4p_x, 4p_y)$.

The classification of the ring and metal orbitals in terms of their symmetries makes it possible to determine the combinations which contribute to the bonding states. Only those ring and metal orbitals which belong to the same representation can contribute to the overall overlap and only these combinations will lead to the formation of a metal–ring bond.

All the remaining combinations are orthogonal. The following orbitals of the cyclopentadienyl (Cp) rings and metal (M) orbitals have the appropriate symmetries: $a_{1g}(Cp) - 4s(M)$; $a_{1g}(Cp) - 3d_{z^2}(M)$; $e_{1g}(Cp) - 3d_{xy, yz}(M)$; $e_{2g}(Cp) - 3d_{xy, x^2-y^2}(M)$: $e_{1u}(Cp - 4p_x(M)$; $a_{2u}(Cp) - 4p_z(M)$. The electronic configuration of the complex can be represented as follows: $[a_{1g}(Cp)]^2$, $[a_{2u}(Cp)]^2$, $[e_{1u}(Cp)]^4$, $[3d_{z^2}(M)]^2$, $[3d_{xy}(M)]^2$, $[3d_{x^2-y^2}(M)]^2$, $[e_{1g}(Cp) - 3d_{xz}(M)]^2$, and $[e_{1g}(Cp) - 3d_{yz}(M)]^2$. (We may note that the energy levels of the electrons in the cyclopentadienyl rings are below the energy levels of the metal electrons.) Since several such combinations are allowed by the symmetry, the determination of the relative contribution of each combination to the metal–ring bond energy requires the calculation of the

overlap integrals and the determination of the relative energies of the combining states.

The principal results of the theoretical calculation are the disposition of the energy levels and the distribution of electron density. In the paramagnetic complexes the outer orbital is half-filled. The magnetic properties of the complex depend on whether the unpaired electron occupies the d_{xy}, $d_{x^2-y^2}$ orbitals (the projection of the orbital moment $M_z = \pm 2$), the d_{xz}, d_{yz} orbitals ($M_z = \pm 1$), or the d_{z^2} orbital ($M_z = 0$). The degeneracy of the d_{xy}, $d_{x^2-y^2}$ and d_{xz}, d_{yz} orbitals should be manifested in the corresponding deviations of the g-factor of the complex from its spin-only value. When the nucleus of the transition metal atom or the nuclei of the ligand atoms have magnetic moments, the hyperfine splittings in the EPR spectra or the magnetic shifts in the NMR spectra can serve as a measure of the unpaired electron density at the corresponding atoms. Fig. 1 illustrates schematically the formation of molecular orbitals by means of a linear combination of the 3d orbitals of the metal and the $2p_z$ orbitals of the carbon atoms of the cyclopentadienyl rings. Fig. 2 presents a diagram of the upper levels of the cyclopentadienyl complexes of Mn, Fe^+, Co, and Ni^+.

II. MAGNETIC PROPERTIES AND THE CHARACTERISATION OF THE EPR AND NMR SPECTRA OF PARAMAGNETIC SANDWICH COMPOUNDS

The study of magnetic susceptibility makes it possible to measure the effective magnetic moment of the molecule, to obtain information about the number of unpaired electrons, and to draw inferences about the properties of the ground state and about the fraction of the orbital component in the measured magnetic susceptibility from the deviation of the effective magnetic moment from the spin-only value. Table 1 presents the magnetic moments of metallocenes and Table 2 those of the diarene complexes.

A change in the oxidation state of the metal atom leads to the transformation of the diamagnetic complexes into paramagnetic complexes and hence permits the application of the EPR method to the study of the electronic structures of sandwich compounds.

A general discussion of the magnetic and magnetic resonance properties of sandwich compounds can be found in the paper of Robertson and McConnell[8]. The characteristics of these compounds are wholly determined by the nature of the central metal atom. In the case of orbital degeneracy (the unpaired electron occupies an e-type orbital), the effective magnetic moment and the g-factor are determined by spin–orbital coupling, by a low-symmetry distortion of the system, and by static and dynamic Jahn–Teller effects. Naturally the contribution of each of the above interactions to the splitting of the degenerate levels is different and depends on the nature of the metal.

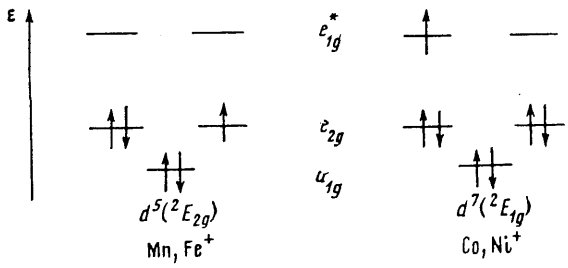


Figure 2. The energy levels of the d electrons in metallocenes.

Table 1. Experimental (μ_{eff}) and spin-only (μ) magnetic moments of metallocenes[8].

Metallocene	μ_{eff}, μ_B	S	μ, μ_B
Vanadocene	3.84	3/2	3.87
Chromocene	3.20	1	2.83
Ferrocenium cation	2.61	1/2	1.73
Manganocene	5.71	5/2	5.91
Cobaltocene	1.76	1/2	1.73
Nickelocene	2.86	1	2.83

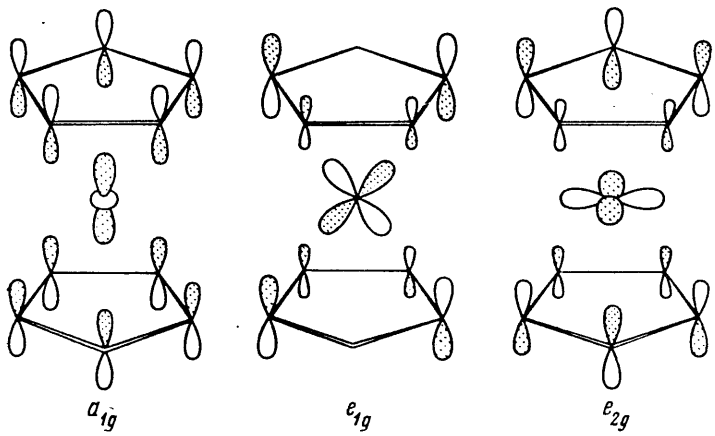


Figure 1. Schematic representation in terms of symmetry characteristics of the valence 3d orbitals of the metal and the molecular orbitals of cyclopentadienyl involved in a linear combination.

For complexes in which the unpaired electrons are distributed among the degenerate orbitals, larger deviations of the g-factor from the value for the free electron are observed. A small splitting of the degenerate levels leads to the appearance of short spin–lattice relaxation times; low temperatures (4–20 K) are required for the observation of EPR in such complexes.

Table 2. Magnetic moments of the diarene complexes of metals[24].

Complex	μ^{*}_{eff}, μ_B	S
Dibenzenevanadium	1.68	1/2
Dimesitylvanadium cation	2.80	1
Dibenzenechromium cation	1.77	1/2
Bishexamethylbenzeneiron cation	1.89	1/2
Bishexamethylbenzeneiron	3.08	1
Bishexamethylbenzenecobalt dication	1.73	1/2
Bishexamethylbenzenecobalt cation	2.95	1
Bishexamethylbenzenecobalt	1.86	1/2
Bishexamethylbenzenenickel dication	3.00	1

*The spin-only moments μ are 1.73 and 2.83 for $S = 1/2$ and $S = 1$ respectively.

The presence of more than one unpaired electron in the molecule leads to the splitting of the levels in a zero external magnetic field as a consequence of the interaction between the unpaired electrons. Such splitting sometimes constitutes an additional difficulty in the observation of EPR. Since zero field splitting can greatly exceed the attainable energy microwave quanta, EPR cannot be observed. In such cases, the observation of EPR is impossible and the application of NMR, which is not subject to the above limitations is particularly valuable. In the NMR spectra of complexes with short electron spin–lattice relaxation times, lines which are relatively narrow for paramagnetic specimens are observed. In the case of systems with a large zero field splitting, NMR is the only feasible microwave spectroscopic research technique.

The hyperfine structure (HFS) of the EPR spectra, the zero field splitting of the signal, and the paramagnetic shift of the NMR lines are important sources of information about the distribution of the unpaired electron density. In the EPR spectra of metallocenes and diarene complexes, a hyperfine structure, which depends on the nature of the metal and is due to the interaction of the unpaired electron with the magnetic moment of the metal nuclei and the ligand protons, is observed. Analysis of the HFS in the solid phase (in single crystals or in vitrified solutions) makes it possible to determine values of the hyperfine interaction (HFI) tensor as well as the isotropic HFI constant which enters into the so-called contact paramagnetic shift of the NMR line.

Under the conditions of rapid electron spin–lattice relaxation, the contact shift $\Delta\nu$(Hz) of the NMR line is described by the equation

$$\Delta\nu/\nu_0 = -Ag_{av}\beta_e S(S+1)/g_N\beta_N(3kT),$$

where A is the constant of the isotropic hyperfine interaction of the unpaired electron with the corresponding nucleus, $g_{av} = 1/3(g_\parallel + 2g_\perp)$, β_e and β_N are the electronic and nuclear magnetons, g_N is the nuclear spectroscopic splitting factor, S the spin of the paramagnetic complex, k the Boltzmann constant, and T the temperature on the Kelvin scale. The above formula shows that the temperature variation of the contact shift is consistent with the Curie law[9]. Hence it follows that only when this law holds is it possible to calculate A from the slope of the plot of $\Delta\nu$ against $1/T$.

The expression for the constant A is

$$A = \frac{8\pi}{6S} g_e\beta_e g_N\beta_N |\psi(0)|^2 ,$$

where $|\psi(0)|$ is the molecular wave function of the unpaired electron at the nucleus. Thus the contact shift carries potentially the same information about the distribution of the unpaired electron density in the paramagnetic complex as the isotropic HFI constant obtained from the EPR spectra. The study of the contact shifts of the NMR lines is of particular value in view of the fact that, apart from the determination of the constant A, it also yields its sign. This permits in its turn the determination of the sign of the spin density at the corresponding atom. The determination of the magnitudes and signs of the spin density permits conclusions concerning the mechanism of the delocalisation of the unpaired electron in the complexes.

When the anisotropy of the g-factor is considerable, the pseudocontact shift[9], arising as a result of the dipole–dipole interaction of the magnetic moment of the unpaired electron with the magnetic moment of the corresponding nucleus at a distance r, makes a contribution, apart from the contact shift, to the experimental paramagnetic shift. The form of the expressions describing the contribution of the pseudocontact shift depends on the ratio of the correlation times of the rotational mobility τ_2 (τ_2 is the time of the rotation of the complex by one radian), the characteristic time determined by the anisotropy of the g-factor, and the electron spin–lattice relaxation time T_1.[10] Two cases are distinguished:

(a) $1/\tau_2 \ll |g_\parallel - g_\perp|\beta H/\hbar$, $T_1 \ll \tau_2$, $\Delta\nu/\nu_0 = \Gamma(g_\parallel^2 - g_\perp^2)/3$;

(b) $1/\tau_2 \gg |g_\parallel - g_\perp|\beta H/\hbar$, $T_1 \ll \tau_2$, $\Delta\nu/\nu_0 = \Gamma(3g_\parallel + 4g_\perp)(g_\parallel - g_\perp)/15$,

where Γ is the so-called geometrical factor taking into account the relative positions of the unpaired electron and the nucleus:

$$\Gamma = -\frac{\beta^2 S(S+1)}{3kT}\left\langle\frac{3\cos^2\varphi - 1}{r^3}\right\rangle .$$

Proton magnetic resonance spectroscopy has been supplemented in recent years by the ^{13}C magnetic resonance spectroscopy. The application of ^{13}C NMR greatly extended the scope of the study of paramagnetic complexes and made it possible to construct a map of the spin density distribution incorporating all the atoms of the complex. Analysis of the spin density distribution makes it possible to estimate the relative involvement of the metal and ligand atoms in the molecular orbital of the unpaired electron, which is important for understanding the nature of the bond in sandwich metal complexes.

1. EPR and NMR Spectra of Sandwich Compounds of Iron

The first EPR spectra of the ferrocenium cation were not obtained until 1969[11], much later than the EPR spectra of the sandwich compounds of other metals. The difficulties in the study of the EPR spectra of ferrocenium and its derivatives are associated with the short spin–lattice relaxation time T_1, which hinders measurements at temperatures above 77 K. The EPR spectra of the ferrocenium cation and its derivatives have been recorded at 20 K in dimethylformamide. Fig. 3 presents the EPR spectra of $Fe(C_5H_5)_2I_3$, $CH_3C_5H_4Fe.C_5H_5I_3$, and $(CH_3C_5H_4)_2FeI_3$. Table 3 presents the values of $g_\parallel$, $g_\perp$, the line widths $\Delta H_\parallel$ and $\Delta H_\perp$, as well as certain

parameters characterising the electronic state of the ferrocenium cation[12]. The line width $\Delta H_\perp$ was measured between the peaks and $\Delta H_\parallel$ was measured at the level of half the height of the signal corresponding to $g_\parallel$. It follows from the data in Table 3 that the introduction of substituents lowers $\Delta H_\perp$ by a factor greater than ten.

Table 3. EPR parameters* of the ferrocenium cation and its derivatives[15].

Substituent	$g_\parallel$	$g_\perp$	$\Delta H_\parallel$, G	$\Delta H_\perp$, G	K	X	δ, cm^{-1}
H	4.35	1.26	140	2500	0.76	1.23	270
CH_3	4.17	1.47	160	1500	0.80	0.92	360
C_6H_5	3.98	1.58	180	850	0.80	0.78	420
1,1'-di-CH_3	3.83	1.67	160	450	0.83	0.66	500
1,1-di-C_4H_9	3.88	1.68	230	600	0.86	0.65	500
C_6H_5CO	3.69	1.73	140	300	0.84	0.58	570
1,1'-di-C_6H_5	3.63	1.74	160	300	0.82	0.57	580
CH_3CO	3.62	1.76	130	220	0.85	0.54	610

*Notation: K is the fraction of the unpaired electron density on the iron atom; $X = \xi/\delta$, where ξ is the spin–orbit coupling constant: δ = energy of the splitting of the e_{2g} level in a low-symmetry field.

Ligand field theory predicts the sequence of the levels of the five degenerate orbitals of the transition metal ion[8], illustrated schematically in Fig. 2. This sequence arises as a result of the influence of the field of the cyclopentadienyl rings on the metal ion orbitals. As a consequence of symmetry properties, the orbital $e_{1g}(3d_{\pm1})$ and $e_{2g}(3d_{\pm2})$ remain degenerate. Since ferrocene is diamagnetic, it has the low-spin configuration $^1A_{1g}(e_{2g})^4(a_{1g})^2$. The distance between the e_{1g} and a_{1g}, e_{2g} orbitals is fairly large and exceeds the exchange interaction energy stabilising the high-spin configuration of the d^6 level.

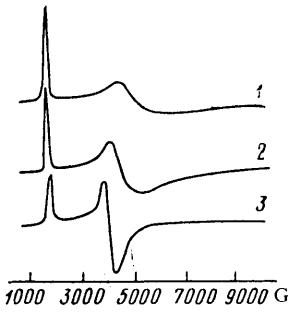


Figure 3. EPR spectra of ferrocenium cations in dimethylformamide at 20 K: 1) $Fe(C_5H_5)_2I_3$; 2) $Fe(C_5H_5)(C_5H_4CH_3)I_3$; 3) $Fe(C_5H_4CH_3)_2I_3$.[15]

Measurement of the magnetic susceptibility of the $FeCp_2^+$ cation showed that it has the low-spin d^5 configuration and that its magnetic moment deviates appreciably from the spin-only value[8]. The orbitally degenerate state $^2E_{2g}(a_{1g})^2(e_{2d})^3$ has been proposed as the ground state of $Fe_2Cp_2^+$.[13,14]

A system of five d electrons has been examined theoretically[15] by replacing it by a single electron "hole" having the electronic configuration $^2E_{2g}(e_{2g})$. In an axial ligand field H_0, this configuration is quadruply degenerate—doubly degenerate for the spin functions α and β and doubly degenerate for the orbital functions e_{+2} and e_{-2}. In view of the axial symmetry of the system, the eigenfunctions of the projection operator of the orbital moment L_z, where the main molecular axis perpendicular to the plane of the ligand rings was selected as the z axis, were chosen as a basis set of wave functions. The spin–orbit interaction $\hat{H}_{SO}$ splits the quadruply degenerate level into two doubly degenerate levels: $\{e_{+2}\alpha, e_{-2}\beta\}$ with $|M_j| = 5/2$ and $\{e_2\alpha, e_{+2}\beta\}$ with $|M_j| = 3/2$. The energies of these states differ by 2ξ, where ξ is the spin–orbit coupling parameter. For the electron "hole", ξ is negative and the doublet with $|M_j| = 5/2$ refers to the ground state of the unpaired electron. This doublet is located several hundreds of cm^{-1} below the doublet with $|M_j| = 3/2$.

$$g_\parallel = 2\langle e_{+2}\alpha|l_z + 2S_z|e_{+2}\alpha\rangle = 2 + 4K\,,$$
$$g_\perp = 2\langle e_{+2}\alpha|l_x + 2S_x|e_{-2}\beta\rangle = 0\,,$$
$$K = \tfrac{1}{2}\langle e_{+2}|l_z|e_{+2}\rangle\,.$$

The result $g_\perp = 0$ implies that, to a first approximation, the levels to which the ground state doublet corresponds are not split by a magnetic field parallel to the x and y axes. On the other hand, the probability of the EPR transitions in the case where the magnetic field is parallel to the z axis is $\langle e_{+2}\alpha|S_x|e_{-2}\beta\rangle = 0$. Hence it follows that the EPR spectrum of the ferrocenium cation should not be observed. On the basis of the results obtained, the author[15] concludes that the symmetry of the cation $FeCp^+$ is lower than the axial symmetry and this explains the presence of the EPR signal.

The decrease of the symmetry of the cation $FeCp_2^+$ may be induced by the solvent molecules, the anion, or the distortion due to the Jahn–Teller effect; in substituted $FeCp_2^+$ the symmetry can also be reduced by the influence of the substituent.

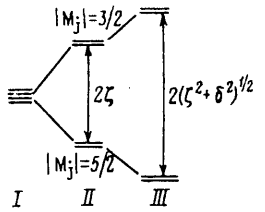


Figure 4. Diagram of the $^2E_{2g}$ levels of the ground state of $Fe(C_5H_5)_2^+$: I) in the axial field of the ligand; II) in the axial field of the ligands with superposition of the spin–orbit coupling (2ξ); III) in the axial field with superposition of spin–orbit coupling and a low-symmetry field (δ).

The overall Hamiltonian $\hat{H}$, describing the behaviour of the unpaired electron, can be represented by the sum of the effective one-electron Hamiltonian $\hat{H}_0$, corresponding to the axial symmetry of the complex, and the terms $\hat{H}_{SO}$ and $\hat{H}_1$ associated respectively with the spin–orbit coupling and the interaction with a low-symmetry field. The latter interaction removes the degeneracy and splits the e_{2g} level into two components, $e_{x^2-y^2}$ and e_{xy}, separated by a distance $\sim 2\delta$. It may be expected that $\hat{H}_1$ and $\hat{H}_{SO}$ are of the same order of

magnitude and that the determination of the splitting requires the solution of the secular equation. The solution of the secular determinant yields two doubly degenerate levels whose location is illustrated in Fig.4.

$$\Psi_1 = (\cos\varphi \cdot e_{x^2-y^2} + i \sin\varphi \cdot e_{xy})\alpha \ ,$$
$$\Psi_2 = (\cos\varphi \cdot e_{x^2-y^2} - i \sin\varphi \cdot e_{xy})\beta \ ,$$

where $\tan\phi = (1 + 1/X^2)^{1/2} - 1/X$ and $X = -\xi/\delta$. The energy of the lower doublet level corresponding to these functions is $-(\xi^2 + \delta^2)^{1/2}$ and the energy of the upper doublet is $+(\xi^2 + \delta^2)^{1/2}$. New values of the g-factors were calculated using these wave functions[15]:

$$g_z = 2\langle\Psi_1|l_z + 2S_z|\Psi_1\rangle = 2 + \frac{4KX}{(1+X^2)^{1/2}} \ ,$$
$$g_x = g_y = 2\langle\Psi_1|l_x + 2S_x|\Psi_2\rangle = \frac{2}{(1+X^2)^{1/2}} \ .$$

The parameters K and X can be determined from the two equations for g_z and $g_x = g_y$.

The orbital $|e_{+2}\rangle$ is a linear combination of the 3d orbital of the iron atom and the ligand π orbital L_π, which is a linear combination of the $2p_z$ orbitals of the carbon atoms in the cyclopentadienyl rings:

$$|e_{+2}\rangle = C_1|3d_{+2}\rangle + C_2|L_\pi\rangle \ .$$

Substitution in the equation for K yields the following expression:

$$K = \frac{1}{2}\langle e_{+2}|l_z|e_{+2}\rangle =$$
$$= C_1^2 + C_1C_2\langle 3d_{+2}|l_z|L_\pi\rangle + \frac{1}{2}C_2^2\langle L_\pi|l_z|L_\pi\rangle \ .$$

As the initial approximation it was assumed that the orbital moment associated with the ligand electrons is to a large extent extinguished[15] and for this reason the last two integrals were assumed to be zero. Hence it follows that $K = C_1^2$. It is seen from the data in Table 3 that the average $K = 0.82$ and $C_1 = 0.91$, which shows that the 3d orbital of the iron atom makes the main contribution to the e_{2g} orbital of the complex and that the unpaired electron is localised mainly at the iron atom. Calculations of the molecular orbitals carried out for ferrocene predict the same results. Values in the range 0.85–0.91 were found for C_1.[2-4]

The splittings of the energy levels in a low-symmetry field $\hat{H}_1$ can be determined from the parameter X. Since $\delta = -\xi/X$ and $\xi = C_1^2\xi_0$, where $\xi_0 = 400$ cm^{-1}, the spin–orbit coupling constant for the Fe^{3+} cation is $C_1 = 0.82$. The results obtained show that the axial symmetry is infringed even in the unsubstituted ferrocenium cation. The high value $\delta = 270$ cm^{-1} leads to the conclusion that the infringement of the symmetry is associated with external factors[15].

The similarity of the energies of the states with $|M_j| = 3/2$ and $|M_j| = 5/2$ explains the short spin–lattice relaxation time of the ground state. The energy difference $\Delta E = 2(\xi^2 + \delta^2)^{1/2}$ of the states with $|M_j| = 5/2$ and 3/2 is 860 cm^{-1} in $FeCp_2^+$, 1200 cm^{-1} in $(CH_3C_5H_4)_2Fe^+$, and 1390 cm^{-1} in $(CH_3COC_5H_4)_2Fe^+$. The order of magnitude of these quantities explains why the EPR signal of $FeCp_2^+$ is too broad to be observed at 77 K, while the EPR spectra of complexes with a higher ΔE can be observed at this temperature.

The magnetic moment of the cation $FeCp_2^+$ has been determined[15] by measuring the magnetic susceptibility ($\mu = 2.61$ μ_B in crystalline powders of ferrocenium salts and by the NMR method from the paramagnetic shift of the solvent protons ($\mu = 2.30$ μ_B). The magnetic moment obtained by NMR is in good agreement with the value calculated from EPR data:

$$\mu = \left\{\frac{1}{3}(g_\parallel^2 + 2g_\perp^2)\,S\,(S+1)\right\}^{1/2}\mu_B = 2.35\mu_B \ .$$

The apparent conflict between the results of the theoretical analysis of the distortion of the axial symmetry of $FeCp_2^+$ and the equality of g_x and g_y obtained from the EPR spectrum is due to the fact that the difference $g_x - g_y$ is proportional to $\xi/\Delta E_i$, where $\Delta E_i = E(e_1g) - E(e_2g) \cong 30000$ cm^{-1} is unduly small compared with the line width in the EPR spectrum.

Simultaneously with Prins' communication[15], the study of Horsfield and Wassermann[16], dealing with the same problem, was published. They investigated the EPR spectra of $FeCp_2^+$ trichloroacetate, picrate, and chloride at 77 K. The g-factors obtained differ appreciably ($g_\parallel \cong 3.20$; $g_\perp \cong 1.80$) from Prins' data[15]. In the subsequent discussion, attention was drawn to the instability of the ferrocenium cation[17,18] and the possible formation of paramagnetic impurities. The additional studies which followed the discussion[18] established that the signals recorded by Horsfield and Wassermann are observed in freshly prepared specimens at 77 K, but, on reducing the temperature to 20 K, the more intense signals with the values of $g_\perp$ and $g_\parallel$ obtained by Prins are recorded[15].

Theoretical calculations and experimental EPR spectra of the ferrocenium cation have shown that the main contribution to the orbital of the unpaired electron of the cation comes from the 3d orbital of the metal atom. The shift of the unpaired electron to the ligands might be indicated by the hyperfine structure of the spectrum due to the interaction with the protons of the cyclopentadienyl rings. Since A_H is much smaller than the width of the EPR line, this information cannot be obtained from the EPR spectrum. It was obtained with the aid of NMR.

Fritz et al.[19] were the first to investigate the NMR of the ferrocenium cation and its alkyl derivatives. They measured the paramagnetic shifts of the signals due to the protons in the cyclopentadienyl ring and the protons of the α-CH_2, β-CH_2, and γ-CH_3 groups in the substituted ferrocenium cation. The paramagnetic shifts $\Delta\nu$ (p.p.m.) measured at a frequency of 100 MHz proved to be small:

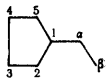
Cp ring	α-CH_2	β-CH_2	γ-CH_3
$-(30-16)$	15 — 18	7	0

The results obtained indicate quantitatively a low unpaired electron density in the ligand orbitals. However, the constants for the isotropic HFI between the unpaired electron and the protons cannot be calculated directly from the paramagnetic shifts because of the contributions to $\Delta\nu$ by the pseudocontact shift. Attempts have been made in a number of studies to separate the contact and pseudocontact contributions[15,19,20]. The inaccuracy of the first attempts was due to the insufficiency of the EPR data and data concerning the structure of the ferrocenium cation[15,19].

It has been found[20] that the dipole contribution to the observed paramagnetic shifts of the signal due to the methyl protons of the cation $Fe(C_5H_4CH_3)_2^+$ is ~55% and the contribution to the paramagnetic shift of the protons of the cyclopentadienyl rings is 25%. The calculated isotropic HFI constants are $A_H = 0.168$ G for $Fe(C_5H_5)_2^+$ and $A_H = 0.161$ G and $A_{CH_3} = 0.095$ G for $Fe(C_5H_4CH_3)_2^+$.

A more thorough analysis of the temperature variation of the paramagnetic shift[21] showed that this variation is different for the protons of the cyclopentadienyl rings of $FeCp_2^+$ and $(RC_5H_5)_2Fe^+$. Whereas in the case of $FeCp_2^+$ the Curie law hold rigorously, deviations are observed for the protons of the $(RC_5H_4)_2Fe^+$ rings. Köhler[21] concluded that the protons in substituted cyclopentadienyl rings are non-equivalent, which leads to the observed deviations in the temperature variation. This hypothesis has been confirmed. The application of ^{13}C NMR showed that the carbon atoms in the cyclopentadienyl rings of $(RC_5H_4)_2Fe^+$ are non-equivalent[22].

Table 4 presents the paramagnetic shifts of the ^{13}C NMR of the ferrocenium cation and some of its alkyl derivatives.



In conformity with the signs of the paramagnetic shifts of the NMR lines of the ^{13}C and ^{1}H nuclei, the signs of the spin density on the corresponding atoms can be obtained. The spin densities on the carbon and hydrogen atoms of the cyclopentadienyl rings have the positive sign. The positive sign of the shift of the proton signal of the CH_3 group in $Fe(C_5H_4CH_3)_2^+$ is due to the fact that the positive pseudocontact shift is greater in absolute magnitude than the negative contact shift[20]. Thus, although the spin densities on the carbon nuclei are in fact positive, the ^{1}H NMR line of the CH_3 group is displaced upfield.

Table 4. Shifts of the ^{13}C NMR lines (p.p.m.) in the spectrum of ferrocenium hexaphosphate in acetone at 28 °C.[22]

Ferrocenium cation	C(1)	C(2, 5), C(3, 4)	C^{α}	C^{β}
$(C_5H_5)_2Fe^+$	—	−314.5	—	—
$(CH_3C_5H_4)_2Fe^+$	−415	−263.0	+10	—
$(C_2H_5C_5H_4)_2Fe^+$	−402.5	−259.8	+0.5	+9.2
$(C_4H_9C_5H_4)_2Fe^+$	−414.0	−233.6 −250.6	−16.3	+3.9

The bis(hexamethylbenzene)iron cation is an example of a 19-electron system (d^7). Three signals, corresponding to three values of the g-factor, are observed in the EPR spectrum: $g_x = 1.865$, $g_y = 1.996$, and $g_z = 2.086$.[23] It is of interest that there is no axial symmetry in such a highly symmetrical molecule. The absorption signal is observed in the range from 25 to 80 K, disappearing at 90 K owing to the considerable broadening of the line. It has been suggested[23] that the unpaired electron occupies the non-bonding ligand orbital e_{2u}. Subsequent study of the NMR spectra of this compound showed that the unpaired electron density on the ligands is low[24]. This result is inconsistent with the hypothesis that the unpaired electron is located in the e_{2u} orbital. It is most likely that the electron occupies the e_{1g}^* orbital of the iron atom.

The electrically neutral arenecyclopentadienyliron complexes also belong to d^7 systems. The reduction of the salts $[AreneFeC_5H_5]^+BF_4^-$ in 1,2-dimethyoxyethane at −70 °C on a sodium mirror leads to the transformation of the d^6 system, isoelectronic with ferrocene, into the d^7 system $a_{1g}^2e_{2g}^4(e_{1g}^*)^1$.[25]

The doubly degenerate e_{1g}^* level is split as a consequence of the low-symmetry interaction with the arene ligand. On the assumption that the unpaired electron occupies mainly one of the two orbitals d_{xz} or d_{yz}, expressions were obtained for $g_{\parallel}$ and $g_{\perp}$:

$$g_z = g_{\parallel} = 2\left(1 - \frac{\lambda_0}{\Delta E}\right);\ g_x = g_y = g_{\perp} = 2,$$

where

$$\Delta E(e_{1g}^*) = E_{d_{xz}} - E_{d_{yz}}, \quad \text{and} \quad \lambda_0(Fe^+) = -350\ cm^{-1}.$$

Table 5 presents the values of $g_{\parallel}$ for electrically neutral arenecyclopentadienyliron complexes (the values of $g_{\perp}$ for all the compounds are close to 2). The table shows that $g_{\parallel}$ decreases in the sequence of ligands benzene, naphthalene, phenanthrene. The values of $\Delta E(e_{1g}^*)$ for benzene, naphthalene, and phenanthrene are respectively 2700, 7700, and 10000 cm^{-1}. The increase of $\Delta E(e_{1g}^*)$ can be attributed to the increase of the electron-donating capacity of the ligands in this sequence, leading to the enhancement of the interaction of the ligands with the iron atom on which there is a positive charge.

Table 5. The values of $g_{\parallel}$ for electrically neutral arenecyclopentadienyliron complexes[25].

Arene	$g_{\parallel}$	Arene	$g_{\parallel}$	Arene	$g_{\parallel}$
Benzene	2.26	Tetralin	2.21	Fluorene*	2.10
Toluene	2.25	Dihydroanthracene	2.22	Naphthalene	2.09
Diphenylmethane	2.24	Mesitylene	2.24	Phenanthrene	2.07
p-Xylene	2.25	Durene	2.21		

*Breakdown of axial symmetry: $g_x = 2.00$; $g_y = 1.99$.

The study of the EPR spectra of the dications $[AreneFeC_5H_5]^{2+}$,[26] obtained by oxidising the initial salts $SbCl_5$ in CH_2Cl_2 at −70 °C, can yield data about the d^5 system which is isoelectronic with the ferrocenium cation[15]. Table 6 presents the values of $g_{\parallel}$, $g_{\perp}$, and $\Delta E(e_{2g}) = E_{d_{x^2-y^2}} - E_{d_{xy}}$:

$$g_z = g_{\parallel} = 2\left(1 - \frac{2\lambda_0}{\Delta E(e_{2g})}\right);\ g_x = g_y = 2;\ \lambda_0 = -400\ cm^{-1}.$$

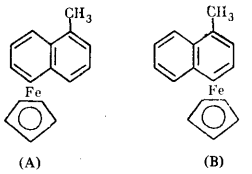
Evidently, the splittings $\Delta E(e_{1g}^*)$ are much greater than $\Delta E(e_{2g})$. This result reflects the greater "π character of the d_{xz} and d_{yz} orbitals and their more effective overlap with the molecular π orbitals of the ligands compared with the $d_{x^2-y^2}$ and d_{xy} orbitals. Comparison of the data in Table 6 with the parameters of the EPR spectra of ferrocenium cations (Table 3) shows that the low-symmetry splitting in the dications $[AreneFeC_5H_5]^{2+}$ is much greater than in ferrocenium cations.

Table 6. The values of $g_{\parallel}$, $g_{\perp}$, and $\Delta E(e_{2g})$ for the EPR spectra of arenecyclopentadienyliron dications[26].

Arene	$g_{\parallel}$	$g_{\perp}$	$\Delta E(e_{2g})$, cm^{-1}
$CH_3OC_6H_5$	3.14	1.940	1400
$C_6H_5OC_6H_5$	3.14	1.920	1400
p-$FC_6H_4C_6H_5$	3.16	1.898	1380
$C_6H_5C_6H_5$	3.04	1.930	1540
$C_{10}H_8$	2.80	1.976	2000
β-$FC_{10}H_7$	2.83	1.976	1930
α-$CH_3C_{10}H_7$ (A)	2.81	1.977	1970
α-$CH_3C_{10}H_7$ (B)	2.71	1.988	2260
$C_{14}H_{10}$	2.86	1.964	1860

It is of interest to compare the data for $[C_{10}H_8FeC_5H_5]^{2+}$, $[\alpha\text{-}CH_3C_{10}H_7FeC_5H_5]^{2+}$, and $[\beta\text{-}FC_{10}H_7FeC_5H_5]^{2+}$. Table 6 shows that the signal corresponding to $g_{\parallel}$ in the $[\alpha\text{-}CH_3C_{10}H_7.FeC_5H_5]^{2+}$ spectrum is split into two components. A smaller splitting is observed also in the signal corresponding to $g_{\perp}$.

We attributed this feature of the $[\alpha\text{-}CH_3C_{10}H_7FeC_5H_5]^{2+}$ spectrum to the existence of two different isomers[26]:



(A) (B)

This hypothesis is confirmed by the NMR data for the cations $[\beta\text{-}CH_3C_{10}H_7FeC_5H_5]^+$ and $[\alpha\text{-}FC_{10}H_7FeC_5H_5]^+$.[27] The ratio of isomers (A) and (B) for the former cation is 55:45 while for the latter cation only isomer (A) is observed.

2. The EPR and NMR Spectra of Sandwich Compounds of Vanadium

The EPR spectrum of VCp_2 has been investigated[28] for a single crystal of diamagnetic $FeCp_2$ and the splitting parameter in a zero magnetic field $D = 0.83$ cm^{-1} was determined for the quartet ground spin state. On the other hand, the EPR spectrum obtained previously[29] in benzene solution at room temperature and consisting of eight well resolved lines ($A_V = 25.6 \times 10^{-4}$ cm^{-1}) with $g = 2.00$ was also attributed to vanadocene. These data are in conflict, since a much greater width of the spectral line recorded in solution is to be expected for such a high value of D.

The EPR spectrum of VCp_2 in vitrified solution in 2-methyltetrahydrofuran has been investigated[30] at 77 K and it has been shown that the signal observed in solution at room temperature is due to an impurity. The VCp_2 signal observed at 77 K is characterised by the parameters $g_\parallel = 2.002$, $g_\perp = 1.99$, $|D| = 2.3$ cm^{-1}, $|A| = 3.7 \times 10^{-4}$ cm^{-1}, and $|B| = 21 \times 10^{-4}$ cm^{-1}.[30] The difference between the given value of $|D|$ and that obtained in another study[29] was attributed[30] to the differences between the matrices in which the EPR spectra of VCp_2 were recorded. The similarity of the measured g-factor to the value for the free electron is consistent with measurements of the magnetic susceptibility and shows that the ground state for vanadium is an orbital singlet $^4A_{1g}$ and corresponds to the configuration $a_{1g}^1 e_{2g}^2$.

On the assumption that a_{1g} is a non-bonding metal orbital, the parameters of the hyperfine interaction tensor can be expressed by the formulae

$$A = A_{iso} - \frac{4}{21}P(2\alpha^2 - 1);\ B = A_{iso} + \frac{2}{21}P(2\alpha^2 - 1),$$

where α is the contribution of the e_{2g} orbital of the metal to the molecular orbital and $P = 2\gamma_e\beta_e\beta_N\langle r^{-3}\rangle$. For $P = 110 \times 10^{-4}$ cm^{-1}, it was found that $\alpha = 0.86$.[30]

Rettig and Drago[9] investigated the NMR spectrum of VCp_2 in toluene at a frequency of 60 MHz and found that the paramagnetic shift of the ring proton signal is −18500 Hz relative to the protons of the diamagnetic dimethylferrocene, i.e. ~300 p.p.m. An estimate of the contribution of the pseudocontact shift showed that it is an insignificant proportion of the overall shift observed experimentally. The temperature variation of the shift obeys the Curie law. The isotropic HFS constant is 0.832 G.

The contact shifts in 1,1-dimethylvanadocene are −20190 G for the protons of the cyclopentadienyl rings and 7195 G for the protons of the methyl group. The constant for the hyperfine interaction with the protons of the methyl group, determined from the NMR data, is 0.323 G.[9]

Comparison of the values and signs of the contact shifts of the ring and methyl group protons has been used[9] to determine the mechanism of the displacement of the unpaired electron density from the metal atom to the ligand. The mechanism of the delocalisation of the unpaired electron in paramagnetic metallocenes proposed previously[13] presupposes the involvement of the 3d orbitals of the metal atoms and the π orbitals of the ligand as well as the spin polarisation of the CH bonds in the ring. The main contradiction between this theory and the experimental data obtained from the NMR spectra of VCp_2 is that the mechanism of the spin polarisation developed by Levy and Orgel[13] in relation to the π-electron free radicals presupposes different signs of the HFI constant for the protons of the CH bond and of the CH_3 group, while their absolute magnitudes are approximately equal. However, in the case of vanadocene the signs of the experimental HFI constants for the ring and methyl group protons are the same, while their absolute values differ greatly—the HFI constant for the ring protons exceeds in absolute magnitude the HFI constant for the methyl group protons by a factor greater than two. The markedly lower HFI constants for the protons of the alkyl substituent compared with the HFI constant for the ring protons had already been noted earlier in a study of the EPR spectra of the cations of alkyl derivatives of dibenzenechromium[31].

Rettig and Drago[9] suggested that the principal mechanism for the transfer of spin density from the central metal atom in individual metallocenes to the ligand protons involves transfer via σ and not π bonds. A characteristic feature of this mechanism is a marked decrease of spin density along the chain of σ bonds and the identical signs of the constants of the hyperfine interaction with the protons of the CH bonds and the CH_3 groups.

^{13}C NMR data for vanadocene and 1,1-dimethylvanadocene have shown that the delocalisation pattern is much more complex[32]. Table 7 presents the contact shifts of the ^{13}C and ^1H NMR signals for vanadocene and its alkyl derivatives. The positive shift of the signal from the ^{13}C atom in the ring implies that the unpaired electron spin density on the ring carbon atoms has a negative sign. The negative sign of the contact shift of the ring protons supports the spin polarisation mechanism and is an argument against the mechanism involving delocalisation via σ bonds.

Table 7. Paramagnetic shifts (p.p.m.) of the ^{13}C and ^1H NMR lines of vanadocene, chromocene, and their alkyl derivatives[32].

Compound	C(1)	C(2,5)	C(3,4)	C^α	C^β	H(2,5)	H(3,4)	H^β	H^γ
$(C_5H_5)_2V$	+588	+588	—	—	—	−315	−315	—	—
$(CH_3C_5H_4)_2V$	+482	+750	+533	−915	—	−326	−326	−116	—
$(C_2H_5C_5H_4)_2V$	+480	+743	+562	−792	−420	−340	−340	−90	−5.4
$(C_4H_9C_5H_4)_2V$	+503	+730	+533	−557	−220	—	—	—	—
$(C_5H_5)_2Cr$	+325	+325	+325	—	—	−324	−324	—	—
$(CH_3C_5H_4)_2Cr$	+68	+505	+347	−535	—	−317	−318	−37.2	—
$(C_2H_5C_5H_4)_2Cr$	+99	+488	+367	−497	−92	−357	−310	−18.0	+3.0
$(C_4H_9C_5H_4)_2Cr$	+130	+483	+368	−390	−22	−344	−312	—	—

The EPR spectra of the diarene sandwich complexes of zerovalent vanadium (with benzene, toluene, mesitylene, and naphthalene as ligands) have been investigated[33]. Hyperfine interaction with the magnetic moment of the vanadium nucleus is observed in the spectra of all these compounds, which leads to the appearance of eight HFS lines ($I_V = 7/2$) with a splitting $A_V = 63$ G. Each of the eight lines in the spectrum of the dibenzenevanadium(O) complex is additionally split into 13 lines with a binomial distribution of relative intensities as a result of the interaction with the protons of

the benzene rings: A_H = 4 G and g = 1.987.[33] The introduction of substituents into the ligands (toluene and mesitylene) does not alter the HFI constants, but merely diminishes the number of lines in the spectrum; hyperfine interaction with the protons of the CH_3 groups is not observed[34].

Analysis of the HFS spectrum of the dinaphthalenevanadium(0) complex showed that only one benzene ring of naphthalene is involved in a bond with the vanadium atom. The spectral parameters (A_V = 63 G, A_H = 4 G, g = 1.987) do not differ from those quoted above for the dibenzenevanadium(0) complex. The electronic configuration $...(e_{1u})^4 (e_{2g})^4 (a_{1g})^1$ with an unpaired electron in the $a_{1g}(3d_{z^2})$ orbital is characteristic of zerovalent vanadium complexes[35].

The results show that the delocalisation of the unpaired electron over the π bonds does not play a significant role in the diarenevanadium(0) compounds.

The paramagnetic shifts of the proton signals of the CH bonds and the CH_3 groups in the ^{1}H NMR spectra of $V(C_6H_6)_2^+$, $V(C_6H_5CH_3)^+$, and $V[C_6H_3(CH_3)_3]_2^+$ [24] (ν_0 = 60 MHz) have been measured:

Compound	$V(C_6H_6)_2^+$	$V(C_6H_5CH_3)_2^+$	$V(C_6H_3(CH_3)_3)_2^+$
A_H, G	1.13	1.34	1.23
δ_H, G	−13 990	−16 740	−16 410
A_{CH}, G	—	0.824	0.306
δ_{CH_3}, Hz	—	−8 400	−3 860

The electronic configuration $(e_{2g})^3 (a_{1g})^1$, corresponding to the degenerate $^3E_{2g}$ ground state, has been proposed on the basis of molecular orbital calculations[36].

3. EPR and NMR Spectra of Sandwich Compounds of Chromium

Nüssbaum and Voitländer[37,38] were unable to observe the EPR signals of the complex $CrCp_2$ either in the 3-cm or 8-mm wavelength range at temperatures from room temperature to 4 K; the reasons for this failure were recognised to be the large zero field splitting and the short relaxation time. The magnetic moment of chromocene greatly exceeds the value of the spin-only magnetic moment, which indicates a degenerate electronic state of the complex. According to theoretical calculations, the ground state of chromocene is $(e_{2g})^3 (a_{1g})^1$ [39] and the a_{1g} level is higher by 0.4 eV than the e_{2g} level.

The paramagnetic shift of the proton signals of chromocene in the NMR spectrum relative to the signals of the dimethylferrocene protons is −18850 Hz (ν_0 = 60 MHz), which corresponds to an HFI constant of 1.23 G.[9] In the spectrum of dimethylchromocene the lines due to the protons of the cyclopentadienyl ring are split into two components, which indicates some redistribution of the unpaired electron density in the cyclopentadienyl rings under the influence of the methyl groups. The shifts of the proton signals of the cyclopentadienyl rings are −18630 and −21896 Hz, while that of the methyl group protons is −2160 Hz. The chemical shifts correspond to the HFI constants A_H = 1.22 and 1.43 G and A_{CH_3} = 0.41 G.

Table 7 lists the contact shifts in the ^{13}C and ^{1}H NMR spectra of chromocene and its alkyl derivatives[32]. As in the case of vanadocene, the contact shift of the lines due to the carbon nuclei of chromocene has a positive sign, which indicates a negative unpaired electron spin density in the cyclopentadienyl ring. In conformity with the CH bond spin polarisation model, the spin density on the hydrogen atoms has a positive sign.

Numerous studies have been devoted to the EPR and NMR spectra of the dibenzenechromium cation and its derivatives. The EPR of dibenzenechromium was observed in 1954.[40] Subsequent investigation[31] showed that the EPR spectrum of the dibenzenechromium cation exhibits a splitting of the lines due to the interaction with both the central atom (the ^{53}Cr isotope) and with the protons of the benzene rings (Fig. 5): $A_{^{53}Cr}$ = 19 G and A_H = 3.6 G. The substitution of hydrogen atoms by methyl groups does not entail splitting by the CH_3 protons. In the case of the isopropyl and cyclohexyl substituents, a splitting of ~1 G by the α-proton is observed[31]. In the spectrum of the cation $[C_6H_2(CH_3)_4]_2Cr$ the splitting by the ring protons increases to 4.34 G.[41]

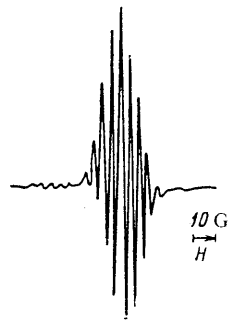


Figure 5. EPR spectrum of the cation $Cr(C_6H_6)_2^+$ in a 1:1 dimethylformamide–chloroform mixture at 200 K.[42]

Analysis of the unpaired electron spin density distribution in the dibenzenechromium cation, assuming delocalisation of the unpaired electron over the π bonds of the ligands, leads to paradoxical results. The employment of the McConnell relation between the splitting A_H and the spin density in the $2p_z$ orbital of the carbon atom ρ_C ($A_H = Q\rho_C$, where Q = −27 G) leads to the conclusion that the overall spin density in the π-electron system of the two benzene rings is approximately equal to two unpaired electrons. On the other hand, the splitting due to the interaction with the ^{53}Cr nucleus in the EPR spectra of inorganic chromium compounds is approximately the same as in the spectrum of the dibenzenechromium cation. This result may be evidence that the unpaired electron in the dibenzenechromium cation is mainly localised at the chromium atom. According to calculations[42], the coefficients α_1, characterising the contribution of the $3d_z$ orbital of the chromium atom to the molecular orbital of the unpaired electron in the dibenzenechromium cation, is close to unity.

Thus the quantitative relations derived on the basis of the study of the π-electron radicals to not hold for the dibenzenechromium cation.

The study of the paramagnetic shifts of the proton signals of the benzene rings and the protons of the methyl groups in the NMR spectra of the dimethyl derivatives of dibenzenechromium cation established the signs of the HFI constants[24,43]. The constant for the splitting by the protons of the benzene ring in the cation $Cr(C_6H_5CH_3)_2^+$ is +3.46 G and that for the splitting by the protons of the methyl groups is −0.46 G.

It has been suggested that the proton HFS is due to the direct interaction of the unpaired electron in the $3d_{z^2}$ orbital with the protons of the benzene ring. Estimates of the contribution of this HFI mechanism showed that it is negligibly small[31,44]. An attempt has been made[24] to explain the observed results by the competition between two mechanisms of the delocalisation of the spin density via π and σ bonds.

As for dinaphthalenevanadium(0), only one naphthalene ring in the dinaphthalenechromium cation is involved in the formation of a bond with the metal. This conclusion is based on the analysis of the proton HFS of the EPR spectrum[35]. The splitting hardly differs from the splittings observed in the spectrum of the dibenzenechromium cation.

4. The EPR and NMR Spectra of Sandwich Compounds of Cobalt

The EPR spectrum of $CoCp_2$ has been investigated at 4 K in a ferrocene single crystal obtained by the joint sublimation of these two compounds[38]. For certain orientations of the crystal, a spectrum with an eight-line HFS, corresponding to the interaction of the unpaired electron with the cobalt nucleus, was recorded. Owing to the uncertainty in the orientation of the crystal, the EPR parameters were not determined accurately: $g_1 = 1.67$, $g_2 = 1.74$, $A = 274$ or 469 MHz, and $B = 274$ or 384 MHz.

More accurate measurements of the EPR parameters of the complex $CoCp_2$ were carried out at 4.2 K in a ruthenocene single crystal: $g_x = 1.140$, $g_y = 1.219$, $g_z = 1.584$, $A_x = +25.5 \times 10^{-4}$ cm^{-1}, $A_y = -120.6 \times 10^{-4}$ cm^{-1}, and $A_z = -103.4 \times 10^{-4}$ cm^{-1}.[42]

Two states have been proposed in accordance with calculations for cobaltocene:

$$(a_{1g}^1)^2(e_{2g})^4(a_{1g}^*)^1 \text{ (Ref.36)}$$

and

$$(a_{1g}^1)^2(e_{2g})^4(e_{2u})^1 \text{ (Ref.3)}$$

The a_{1g}^* orbital is the virtually pure 4*s* orbital of the metal. In this case the constant for the hyperfine interaction with the cobalt nucleus should be ~4800 MHz,[9] whereas the experimental value is ~300 MHz. The hypothesis that the unpaired electron is located in the non-bonding e_{2u} orbital of the ligand, which does not interact with the cobalt orbital by virtue of symmetry considerations, should lead to a vanishingly weak hyperfine interaction with the cobalt nucleus. The ground state $(e_{2g})^4(a_{1g}^1)^2(e_{1g}^*)^1$ is consistent with the EPR data[38]. It has been shown that spin–orbit coupling, orthorhombic distortion, and the dynamic Jahn–Teller effect influence the EPR parameters of the orbitally degenerate $^2E_{1g}$ ground state of cobaltocene. The e_{1g}^* orbital of the unpaired electron is determined to the extent of 58% by the 3*d* orbital of the metal and 42% by the π orbital of the ligand.

The contact shift in the ^{1}H NMR spectrum of $CoCp_2$ is +3230 Hz ($\nu_0 = 60$ MHz) and $A_H = -1.01$ G. The ring protons in $Co(C_5H_4CH_3)_2$ are non-equivalent and two lines with shifts of +2917 and 4305 Hz and $A_H = -0.904$ and -1.34 G are observed. The shift of the line of the CH_3 protons is -687 Hz with $A_{CH_3} = 0.214$ G.[9]

The data in Table 8, which presents the contact shifts of the ^{13}C and ^{1}H NMR lines of cobaltocene and its alkyl derivatives, make it possible to follow the characteristics of the spreading of the spin density from the metal atom to the ligand atoms. The signs of the shifts show that the spin density is positive on the carbon atom and negative on the hydrogen atoms of the rings[32].

A large upfield shift of +3535 Hz is observed in the NMR spectrum of the cation $Co(C_6H_6)_2^+$. The substitution by the methyl group in $Co(C_6H_5CH_3)_2^+$ leads to a shift of the line due to the methyl protons by -2650 Hz.[24] The directions and magnitudes of the ring and methyl proton line shifts indicate the predominance of the mechanism involving the delocalisation of the unpaired electron density via the π bonds. The lines of the CH_3 protons in the $Co[C_6(CH_3)_6]_2^+$ spectrum are displaced downfield by 3695 Hz with $A_H = 0.308$ G.

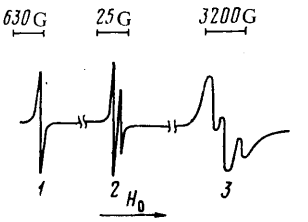


Figure 6. ^{1}H NMR spectrum of the ditoluenecobalt cation in toluene at 298 K: 1) line of the methyl protons of the cation; 2) line of the protons in the solvent molecules; 3) line of the protons in the benzene ring of the cation[24].

When a methyl group is introduced, the lines due to the protons of the benzene rings in the $Co(C_6H_5CH_3)_2^+$ spectrum are split into three signals. Fig.6 shows that the relative intensities of these signals are 2:2:1. These lines have been attributed[24] to the *ortho*- and *meta*-protons (overall intensity 4) and to the proton in the *para*-position (intensity 1). The nature of the splitting of the ring proton lines has been compared with the HFS and the distribution of the unpaired electron density in the toluene radial-anion[46]. Together with the similarity of the spectroscopic data for $Co(C_6H_5CH_3)_2^+$ and $C_6H_5CH_3^-$ (approximate equivalence of the *ortho*- and *meta*-protons and their difference from the *para*-proton), there is also a significant difference, which consists in the fact that the constant for the hyperfine interaction with the proton in the *para*-position in the toluene radical-anion is approximately nine times smaller than the constant for the hyperfine interaction with the protons in the *ortho*- and *meta*-positions. On the other hand, the ratio of these constants in the ^{1}H NMR spectrum of the cation $Co(C_6H_5CH_3)_2^+$ is close to unity. The HFI constant for the protons of the methyl group in the toluene radical-anion is approximately ten times smaller than the HFI constants for the *ortho*- and *meta*-protons. The corresponding quantities for $Co(C_6H_5.CH_3)_2^+$ are of the same order of magnitude and have the same signs, which implies that there is no significant redistribution of the unpaired electron density in the π-electron system of the benzene rings in $Co(C_6H_5CH_3)_2^+$ compared with $Co(C_6H_6)_2^+$.

III. NMR SPECTRA OF NICKELOCENE

McConnell and Holm[47] were the first to observe the proton magnetic resonance of solid nickelocene. The large shift of the NMR proton line which they noted was the first example of the observation of what is nowadays well known as a contact shift.

The EPR spectrum of nickelocene has not been observed in the wavelength range 3.0–0.8 cm and at temperatures from 77 to 4 K.[37] Measurements of the magnetic susceptibility showed that $g_\parallel = 2.0023$, $g_\perp = 2.06$, and the zero-field splitting constant $D = 25.6$ cm^{-1}.[48] Consequently, the magnetic fields and bond lengths used by Nüssbaum and Voitländer[37] were insufficient for the observation of the EPR of nickelocene.

In the ground state of nickelocene $(a_{1g}^1)^2(e_{2g})^4(e_{2u})^2$, proposed on the basis of theoretical calculations, two unpaired electrons are located in the ligand orbital e_{2u}.[3] However,

the large splitting of the signals in a zero field shows that both unpaired electrons are located at the metal atom. It is known that the zero-field splittings or organic triplet molecules are much smaller[49].

The states

$$(a_{1g}^1)^2(e_{2g})^4(e_{1u}^*)$$

and

$$(a_{1g}^1)^2(e_{2g})^4(e_{1g}^*)^2$$

have been proposed for nickelocene on the basis of a study of the magnetic susceptibility[48]. The first state includes the metal $4p_x$ and $4p_y$ orbitals as carriers of the unpaired electron, while in the second the unpaired electron is in the d_{xz} and d_{yz} orbitals. NMR data are consistent with the second state.

Table 8. Paramagnetic shifts (p.p.m.) of the ^{13}C and ^1H NMR lines of cobaltocene, nickelocene, and their alkyl derivatives[32].

Compound	C(1)	C(2, 5)	C(3, 4)	C^α	C^β	H(2, 5)	H(3, 4)	H^β	H^γ
$(C_5H_5)_2Co$	−577	−577	−577	—	—	+56.2	+56.2	—	—
$(CH_3C_5H_4)_2Co$	−358	−437	−755	+112	—	+49.0	+73.6	−12.2	—
$(C_2H_5C_5H_4)_2Co$	−337	−433	−705	+112	−56	—	—	−13.6	−2.4
$(C_4H_9C_5H_4)_2Co$	−458	−458	−633	+94	−123	+50.2	+64.0	—	−2.7
$(C_5H_5)_2Ni$	−1436	−1436	−1436	—	—	+263	+263	—	—
$(CH_3C_5H_4)_2Ni$	−1285	−1475	—	+640	—	+263	+263	−210	—
$(C_2H_5C_5H_4)_2Ni$	—	—	—	+603	−475	+257	+257	−203	−4.5

The study of the ^1H NMR spectra of $NiCp_2$ and $Ni(C_5H_4CH_3)_2$ in solution in toluene at a frequency of 60 MHz and 298 K showed that the ring proton line is displaced by +15300 Hz in the $NiCp_2$ spectrum and by +15190 Hz in the $Ni(C_5H_4CH_3)_2$ spectrum, while the CH_3 proton line is displaced by 11900 Hz. The calculated HFI constants are $A_H = -1.24$ and -1.23 G and $A_{CH_3} = 0.96$ G.[9] Table 8 lists the ^{13}C and ^1H NMR data for nickelocene and its alkyl derivatives. The spin density at the ring carbon atom has the positive sign and that at the ring hydrogen atoms has the negative signs. Comparison of the signs and magnitudes of the contact shifts for the ring and methyl protons shows that the mechanism involving delocalisation via π bonds is most clearly manifested in nickelocene.

IV. EPR SPECTRA OF MANGANOCENE

Depending on the axial splitting (i.e. on the ligand field strength) and on the splitting in a zero magnetic field, the complex $MnCp_2$ can exist in two states: in the high-spin state $(a_{1g}^1 e_{2g}^2 e_{1g}^2)\,^6A_{1g}$ and in the low-spin state $(a_{1g}^2 e_{2g}^3 g)\,^2E_{2g}$ or $(a_{1g}^1 e_{2g}^4 g)\,^2A_{1g}$. Pure $MnCp_2$ gives rise to a broad EPR signal with $g = 2$, which completely disappears on cooling to 4.2 K.[50]

The environment of $MnCp_2$, which arises on its joint crystallisation with various diamagnetic molecules, has a considerable influence on the form of its EPR spectrum[51]. Manganocene in the $MgCp_2$ lattice exhibits at 4.2 K and a frequency of 9.5 GHz a spectrum characteristic of a high-spin d^5 system with $g \cong 2$, the splitting due to the hyperfine interaction with the ^{55}Mn nucleus being characterised by the constant $A = 65$ G and the order of magnitude of the splitting in a zero magnetic field being equal to the order of magnitude of the applied quantum ($0.3\ cm^{-1}$).

In other isostructural lattices ($FeCp_2$ and $RuCp_2$) manganocene exhibits completely different EPR spectra, which characterises it as a low-spin system. The low-spin $MnCp_2$ state $^2E_{2g}$ is isoelectronic with the state of the ferrocenium cation. As for the ferrocenium cation, a strong anisotropy of the g-factor is observed ($g_\parallel = 3.519$, $g_\perp = 1.222$, $A_\parallel = 52.3 \times 10^{-4}\ cm^{-1}$, and $A_\perp = 26 \times 10^{-4}\ cm^{-1}$ for the $FeCp_2$ lattice)[51]. As in the case of the ferrocenium cation, the introduction of substituents into the cyclopentadienyl ring decreases the anisotropy of the g-factor.

In the $Fe(C_5H_4CH_3)_2$ crystal, the g-factor for the complex $Mn(C_5M_4CH_3)_2$ has the following values: $g_\parallel = 3.06$ and $g_\perp = 1.850$ ($A_\parallel = 11.4 \times 10^{-4}\ cm^{-1}$ and $A_\perp = 24.5 \times 10^{-4}\ cm^{-1}$).[51]

None of the low-spin $MnCp_2$ states gave rise to EPR signals on heating above 77 K. The low-symmetry splitting is $\delta = 200\ cm^{-1}$ for $MnCp_2$ and $\delta = 630\ cm^{-1}$ for $Mn(C_5H_4CH_3)_2$. The spin–orbit coupling parameter is $\xi = 260\ cm^{-1}$.[51]

The results obtained show that the energies of the low- and high-spin states of manganocene differ by a small amount and weak intermolecular forces are sufficient to alter the ground electronic configurations. The lattices which promote the formation of longer metal–ring bonds favour the appearance of the high-spin system and conversely those promoting the formation of shorter bonds favour the appearance of the low-spin system. The "distance" between these two states is ~0.5 kcal mol^{-1}.[51]

V. THE JAHN–TELLER EFFECT IN SANDWICH COMPOUNDS

In those cases where the orbital state of the ion is degenerate because of symmetry factors, the ligands are acted upon by forces which distort the distribution of the nuclei until the ion assumes a configuration having both a lower symmetry and a lower energy; the existing degeneracy is thereby eliminated (the Jahn–Teller effect). The theory of the Jahn–Teller effect and its manifestation in the EPR spectra of coordination compounds have been described in monographs[52,53].

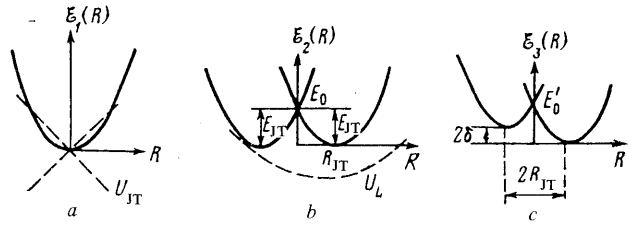


Figure 7. Schematic representation of sections through potential surfaces: *a*) for an orbitally non-degenerate complex; *b*) and *c*) section along the active Jahn–Teller coordinate of a doubly orbitally degenerate complex.

The electronic rearrangements arising as a result of the Jahn–Teller effect can be accounted for qualitatively by considering the potential energy surfaces (Fig. 7). In contrast to the orbitally non-degenerate complexes [$\mathscr{E}_1(R)$, Fig. 7*a*], in an orbitally degenerate complex there are several equivalent potential energy minima stabilised by the energy associated with the Jahn–Teller effect (E_{JT}) and displaced by an amount R_{JT} relative to the nuclear configuration corresponding to the maximum symmetry of the complex [$\mathscr{E}_2(R)$, Fig. 7*b*]. The curves in Fig. 7*b* have been obtained from the plot illustrated in Fig. 7*a* by adding to the $\mathscr{E}_1(R)$ potential energy curve the linear potential U_{JT} with the opposite slope.

The superposition of the weak asymmetric perturbing potential U_L (for example, the field of the surrounding molecules) onto the symmetrical potential $\mathscr{E}_2(R)$ leads to the appearance of an asymmetric potential $\mathscr{E}_3(R)$ (Fig.7c).

Potential surfaces known as the "sombrero" or "Mexican hat" surfaces correspond to octahedral complexes whose symmetry has been distorted by the Jahn–Teller effect. The shape of the surface is determined by the interaction of the doubly degenerate electronic E level with the doubly degenerate e vibration. Such a surface is obtained by rotating the potential energy curve illustrated in Fig.7b about the ordinate axis. The geometrical locus of the points orresponding to the energy minimum is a circumference with the radius R_{JT}.[53] Allowance for the quadratic terms in the Jahn–Teller potential leads to an increase in the complexity of the form of the potential surface and to the appearance of three minima on the above circumference, corresponding to distortions of the octahedra along three different axes. Fig.8 illustrates an expanded section through the lower surface for the E level of the octahedral complex; both the energy of the vibrational quantum $\hbar\omega$ and the tunnel splitting Δ, determining the probability of the transition between the minima, are shown. The manifestation of the Jahn–Teller effect in the EPR spectra depends on the ratios of E_{JT}, $\hbar\omega$, and Δ.

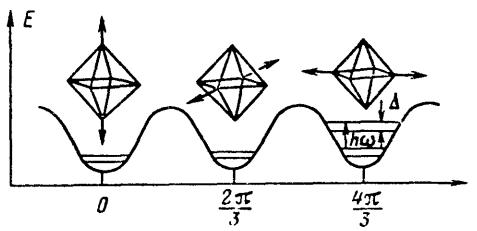


Figure 8. Potential surface corresponding to the distortions of an octahedral complex along three axes: $\hbar\omega$ = energy of vibrational quantum; Δ = tunnel splitting.

Numerous data on the manifestation of the Jahn–Teller effect in the EPR spectra have been obtained for crystals containing the Cu^{2+} ion. The characteristic features of this manifestation are as follows. At high temperatures the spectrum is characterised by an isotropic g-factor of ~2.2. As the temperature is reduced, the form of the spectrum changes reversibly with temperature in a certain transition region. The temperature range in which this occurs is different for different salts and is usually below 60 K, most frequently in the range from 40 to 4 K. At temperatures below the transition region three different spectra with anisotropic g-factors ($g_\parallel \cong 2.4$, $g_\perp \cong 2.1$) are observed; these spectra have axial symmetry relative to each of three mutually perpendicular fourfold axes of the complex CuY_6. A characteristic feature of the behaviour of the spectrum in the transition region is the simultaneous existence of anisotropic and isotropic spectra. With increase of temperature, the intensity of the lines of the first spectrum falls and that of the second increases.

Within the framework of the qualitative description of the Jahn–Teller effect presented above, the temperature-induced changes in the spectra of CuY_6 are described as follows. If $E_{JT} > \hbar\omega$ and the temperature is below the transition region, then the distortion of the octahedron is stable. The system is in one of the minima. Since an increase in the length of one of the three axes of the octahedron takes place at random, the observation of three anisotropic spectra corresponds to their random orientation relative to the direction of the magnetic field. An increase of temperature leads to the population of the excited vibrational states. Whereas the tunnel splitting is small in the zeroth vibrational level, in the excited states it increases sharply, as a result of which the distortion of the complex ceases to be stable and begins to move along its axes. If the quantity $\gamma_e(g_\parallel - g_\perp)\mu_\sigma H$ (γ_e is the gyromagnetic ratio of the electron) is smaller than $1/\tau$ (the rate of transition between equivalent distortions), then one line corresponding to $\bar{g} = 1/3(g_\parallel + 2g_\perp)$ will be recorded in the spectrum. On the other hand, if $E_{JT} < \hbar\omega$, the distortion is unstable within the limits of a single minimum however low the temperature. The Jahn–Teller effect influences not only the form of the EPR spectrum but also the g-factors and the HFI constants.

The influence of the Jahn–Teller effect on the low-spin d^5 and d^7 states of metallocenes has been investigated in studies[54,55] dealing with cobaltocene, manganocene, ferrocenium cations, and nickelocenium cations. Paramagnetic complexes have been investigated in a large number of different diamagnetic crystal lattices in order to estimate the influence of the asymmetric environment on the parameters of the spin-Hamiltonian. For all the orbitally degenerate d^5 and d^7 complexes, an appreciable dependence of the g-tensor on the structure of the crystal lattice has been observed. On the other hand, the absence of the sensitivity by the magnetic parameters to the molecular environment is characteristic of orbitally non-degenerate complexes [vanadocene, $d^3(^4A_{1g})$].

When the Jahn–Teller effect is taken into account, the g-factor is found to depend on the selected orbital moment quenching factor V in addition to its dependence on the low-symmetry distortion δ. The formula quoted above assumes the following form for g_z of the ferrocenium cation with allowance for V: $g_z = 2 + 4KXV/(1 + X^2)^{1/2}$. In the absence of the Jahn–Teller effect, $V = 1$, tending to zero in the case of a strong linear Jahn–Teller effect. For the separate determination of KV and $X = -\zeta/\delta$, Ammeter and coworkers[54,55] used terms of the spin-Hamiltonian other than g_z. The determination of the factor V as a function of the parameter δ in various crystal lattices showed that the dynamic Jahn–Teller motion of a free molecule is suppressed by the increasing asymmetric fields of the matrix. Systematic variation of the lattice structure and the introduction of substituents into the cyclopentadienyl ring made it possible to observe a gradual transition from the purely dynamic Jahn–Teller effect to the limiting case of a static distortion of the complexes. Extrapolation to the case of a free molecule ($\delta = 0$) shows that, for all the orbitally degenerate systems investigated, the distortion of the C_5H_5 rings remains fully dynamic, i.e. the Jahn–Teller stabilisation energy E_{JT} does not exceed the energy of the quantum $\hbar\omega$ corresponding to the active vibration. Ammeter and coworkers[54,55] considered different types of vibrations and indicated those which are active as regards the formation of a linkage between the electronic and vibrational motions.

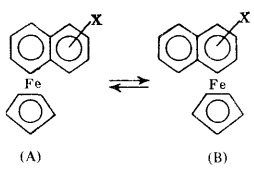
There are indications of the possibility of the existence also of the static Jahn–Teller effect in metallocenes. X-Ray diffraction analysis of decamethylferrocene $[d^6(^1A_{1g})]$ and decamethylmanganocene $[d^5(^2E_{2g})]$ revealed a distortion of the symmetry for the orbitally degenerate manganocene complex[56].

A pattern analogous to that observed in the case of Cu^{2+} ions has been observed in the study of the EPR spectra of naphthalenecyclopentadienyliron[57]. The anisotropic signal at 77 K ($g_\parallel = 2.09$, $g_\perp = 2.006$) is converted into an isotropic signal at 150 K with $\bar{g} = 1/3(g_\parallel + 2g_\perp)$. Averaging of the anisotropy of the g-factor with increase of temperature has

also been observed for other arenecyclopentadienyliron complexes near the melting point of 1,2-dimethoxyethane (−70 °C), in which these complexes have been obtained by reducing the corresponding cations with sodium[25].

The possibility of the manifestation of the Jahn–Teller effect in arenecyclopentadienyliron complexes is determined by the quasi-degenerate nature of the iron states $d^7(^2E_{1g})$, split owing to the low-symmetry interaction with the arene ligand. A characteristic feature of the chemical bond in the given compounds compared with the dicyclopentadienyl compounds consists in the fact that the symmetries of the molecular wave functions of the arene and cyclopentadienyl ligands are different. For this reason, the common molecular orbitals leading to the formation of a chemical bond are formed only from the fully symmetrical molecular orbitals of the ligands. Other (higher) occupied orbitals consist only of combinations of the atomic orbitals of the iron atom with the molecular orbitals of the cyclopentadienyl ring[58]. In the fully symmetric molecular wave function of naphthalene, the maximum electron density corresponds to the 9- and 10-positions and one can assume that an energy minimum in the neutral complex corresponds to the symmetrical position of the iron atom when no account is taken of the Jahn–Teller effect. The distortion of this symmetrical structure associated with the shift of the iron atom towards the centre of one of the benzene rings of naphthalene can lead to the appearance of two potential energy minima located symmetrically relative to the bond between the carbon atoms in the 9- and 10-positions. The tunnelling of the iron atom between these two minima in combination with the rotation of the naphthalene ligand about the bond between naphthalene and the iron atom should lead to the averaging of the anisotropy of the g-factor.

In order to confirm the above model of motion, the EPR spectra of α-$CH_3C_{10}H_7FeC_5H_5$ and β-$FC_{10}H_7FeC_5H_5$ were obtained[57]. At 77 K their spectra do not differ from that of $C_{10}H_8FeC_5H_5$. With increase of temperature, the $g_\parallel$ signals in the spectra of α-$CH_3C_{10}H_7FeC_5H_5$ and β-$FC_{10}H_7FeC_5H_5$ are split into two components. The appearance of two $g_\parallel$ signals was attributed to the existence of two isomers (A) and (B):



At 77 K only the single isomer (A) exists, being the most stable, while with increase of temperature the isomer (B) also arises as a result of the migration of the iron atom. The quantity $g_\parallel^A - g_\parallel^B$ corresponds to the energy difference $\Delta E_{AB} \cong 200$ cm^{-1}. The energy of the vibrational quantum (300 cm^{-1}) and the tunnel splitting (1 – 3 cm^{-1}) were determined from the temperature variation of the EPR spectrum of $C_{10}H_8FeC_5H_5$.[57]

VI. THE ELECTRONIC STRUCTURE OF METALLOCENES AND THE MECHANISM OF SPIN DELOCALISATION

In combination with electronic absorption spectroscopic, photoelectron spectroscopic, and γ-spectroscopic data as well as the results of quantum-chemical calculations, the magnetic resonance data presented make it possible to describe fairly completely the entire scheme of the energy levels of metallocenes and fit qualitatively quite well within the general sequence of the energy levels of metallocenes: $a_{1g} \leqslant e_{2g} \ll e_{1g}^*$. A quantitative description of the above scheme based on experimental data is impossible in the absence of theoretical analysis.

The d–d transition bands in the electronic absorption spectra of the d^6 metallocenes $Fe(C_5H_5)_2$, $Ru(C_5H_5)_2$, and $Co(C_5H_5)_2^+$ were analysed within the framework of the ligand field theory[59]. The following one-electron parameters characterising the energy level scheme were obtained: $\Delta_1 = \varepsilon(e_{2g}) - \varepsilon(a_{1g}) = 7000$ cm^{-1} and $\Delta_2 = \varepsilon(e_{1g}^*) - \varepsilon(a_{1g}) \cong 22000 - 30000$ cm^{-1}. The result $e_{2g} < a_{1g}$ conflicts with the EPR data for ferrocenium, the ground state of which is $^2E_{2g}$. According to non-empirical calculations for ferrocene, $e_{2g} > a_{1g}$.[60] Within the framework of non-empirical calculations for ferrocene, considerable differences (10000 cm^{-1}) arise on comparing the energies of the d–d transition bands with the differences between the total energies of the ground and excited states and the difference between the energies of the "frozen" molecular orbitals. Although the first method is more rigorous, it is difficult to give preference to it from the standpoint of agreement with experiment[60]. In the theoretical analysis of the ionisation potentials, the above differences reach approximately 6 eV, which makes it necessary to treat with caution the estimate of the distance between different orbitals from the difference between the ionisation potentials (the Koopmans theorem). The principal source of the large differences is the contribution of the electronic relaxation and of the energy of the rearrangement of the electron cloud on ionisation of the complex[61].

Analysis of the charge-transfer bands makes it possible to estimate the distance from the energy levels of the metal to the levels of the ligand[59,60]. The bands of the d–d transitions between the a_{1g}, e_{2g}, and e_{1g}^* orbitals and the charge-transfer bands are in the visible and ultraviolet regions. According to the available data, the possible transitions between the a_{1g} and e_{2g} orbitals occur in the red and infrared regions. One of the infrared bands (200 cm^{-1}) in the ferrocenium spectrum has been assigned to the electronic transition between the $^2E_2$ and $^2A_1$ states[62].

Thus the fundamental energy level scheme for sandwich compounds has now been firmly established and is quite fully characterised in quantitative terms. A compilation of the electronic states of certain complexes, based on the analysis of theoretical and experimental data, has been published[24] (Table 9).

Table 9. The electronic configurations of various metallocenes and diarene complexes.

Complex	No. of d electrons	Electronic configuration	Ground state
$V(Cp)_2$	3	$(e_{2g})^2(a_{1g})^1$	$^4A_{1g}$
$Cr(Cp)_2$	4	$(e_{2g})^3(a_{1g})^1$	$^3E_{2g}$
$V(C_6H_6)_2^+$	4	$(e_{2g})^3(a_{1g})^1$	$^3E_{2g}$
$Cr(C_6H_6)_2^+$	5	$(e_{2g})^4(a_{1g})^1$	$^2A_{1g}$
$Fe(Cp)_2^+$	5	$(a_{1g})^2(2_{2g})^3$	$^2E_{2g}$
$V(C_6H_6)_2$	5	$(e_{2g})^4(a_{1g})^1$	$^2A_{1g}$
$Cr(C_6H_6)_2$	6	$(e_{2g})^4(a_{1g})^2$	$^1A_{1g}$
$Fe(Cp)_2$	6	$(e_{2g})^4(a_{1g})^2$	$^1A_{1g}$
$Fe(C_6(CH_3)_6)_2^+$	6	$(e_{2g})^4(a_{1g})^2$	$^1A_{1g}$
$Co(Cp)_2$	7	$(e_{2g})^4(a_{1g})^2(e_{1g})^1$	$^2E_{1g}$
$Fe(C_6(CH_3)_6)_2^+$	7	$(e_{2g})^4(a_{1g})^2(e_{1g})^1$	$^2E_{1g}$
$Ni(Cp)_2$	8	$(e_{2g})^4(a_{1g})^2(e_{1g})^2$	$^3A_{1g}$
$Co(C_6(CH_3)_6)_2^+$	8	$(e_{2g})^4(a_{1g})^2(e_{1g})^2$	$^3A_{1g}$
$Ni(C_6(CH_3)_6)_2^+$	8	$(e_{2g})^4(a_{1g})^2(e_{1g})^2$	$^3A_{1g}$

The most complex problem in the description of the electronic structure of the compounds considered here is the mechanism of the delocalisation of spin density. The attempts undertaken hitherto at the calculation of the distribution of spin density cannot be regarded as satisfactory,

because they were based solely on the idea of the competition between processes involving delocalisation via the π and σ bonds[63]. ^{13}C NMR data for metallocenes showed that the delocalisation pattern is more complex. It is seen from a comparison of the ^{13}C NMR spectra of various metallocenes that, depending on the nature of the metal, not only the magnitude but also the sign of the paramagnetic shift changes. Whereas the shift is negative for nickelocene and cobaltocene, it is positive for vanadocene and chromocene, which corresponds to a negative spin density of the unpaired electron on the carbon atom. Although the signs of the shifts of the proton signals of metallocenes are correlated with the signs of the shifts of the ^{13}C nuclei in accordance with the McConnell equation, a quantitative correspondence is not observed.

In order to account for the magnitude of the ^{13}C shifts, it was suggested that one assumes that they are determined by the sum of three contributions[64]:

$$\sigma^{c}_{obsd} = \sigma^{\pi}_{con} + \sigma^{\sigma}_{con} + \sigma_{dip} ,$$

where the σ^{π}_{con} contribution is of a complex type. It can include directly the unpaired electron density due to the exchange interaction between the 3*d* orbitals of the metal and the $2p_z$ orbitals of the ligands. This situation apparently arises in nickelocene and cobaltocene. However, the spin density can be displaced onto the carbon atoms also via a different pathway resulting from an indirect polarisation mechanism. The polarisation mechanism operates in those cases where the degree of direct conjugation is slight or zero. According to the theory[65], the interaction of the unpaired electron with the electrons in the occupied orbitals results in the motion of electrons with α- and β-spins in somewhat different orbitals. The summation of the spin densities over all the occupied orbitals results in the possibility of the appearance of a spin density at an individual atom with both positive and negative signs. It is believed[64] that the polarisation of the atomic orbitals of the metal and their interaction with the π orbitals of the ligands leads to the appearance of a negative spin density on the carbon atoms in vanadocene and chromocene.

Although the exchange polarisation does predominate in the transfer of spin density to the carbon atoms of vanadocene and chromocene, the available data show that there is a simultaneous direct delocalisation of the positive spin density via the σ orbitals, which leads to a negative contribution to the shift of the ^{13}C NMR lines. This effect is manifested by a smaller ratio of the shifts of the ^{13}C and ^{1}H lines, which is −2 for vanadium compared with −4.5 for nickel[64].

Direct exchange between the 3*d* electrons of the metal and the σ orbitals located in the plane of the cyclopentadienyl rings should lead to higher HFI constants as a consequence of the significant *s* character of these orbitals. The pseudo-contact contribution is apparently small for vanadocene and chromocene, since they are in the *A* states and the degree of anisotropy of their *g*-factors is small. However, this contribution can be appreciable for chromocene and cobaltocene.

The separation of the contributions determining the HFI constants and the contact shifts of the ^{13}C and ^{1}H lines is important for the understanding of the nature of the aromaticity and the properties of the π-electron system of the complexes investigated, particularly in the case of substituted metallocenes and diarene complexes. The results exhibit significant differences between the properties of the free ligands and the ligands in the complexes.

Measurements were made of the paramagnetic shifts in the ^{13}C and ^{1}H NMR spectra of symmetrical polymethyl-substituted ferrocenium cations. The isolation of the contact (Fermi) and pseudo-contact (dipole–dipole) terms showed that the signs of the contact shifts for the carbon atoms of the cyclopentadienyl rings vary in a complex manner as a function of the number and positions of the methyl groups[66,67]. When one methyl group is introduced, the sign of the contact shift changes from negative to positive only at the carbon atom linked to the CH_3 group. When four methyl groups are introduced, the contact shifts at all the carbon atoms, with the exception of the unsubstituted atom, acquire positive signs. If the number of methyl groups in the cyclopentadienyl ring is 0, 2, 3, and 5, then a negative contact shift is characteristic of all the carbon atoms in the ring. In order to explain the complex distribution of spin density, it proved necessary to take into account, apart from the competition between different delocalisation mechanisms mentioned above, the thermal population of the close vacant *d* orbitals by the unpaired electron and the influence of the splitting of the degenerate levels of the molecular π orbitals of cyclopentadienyl under the influence of substituents.

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The analysis of the experimental and theoretical studies on sandwich compounds indicates a considerable progress in the understanding of the nature of the complex organometallic chemical bond. The many-electron nature of this bond determines the existence of a large number of interesting effects, vigorous investigation of which is being continued.

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A Hydrodynamic Invariant of Polymeric Molecules

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Theories of the hydrodynamic properties of macromolecules in solution are examined, from which the invariant relation $A_0 = k\eta_0(M[\eta]/100)^{1/3}f$ can be obtained between the intrinsic viscosity $[\eta]$, the molecular mass M, and the coefficient of sliding friction of the molecule f. Analysis of the experimental results will indicate the most probable values of the invariant A_0 for various classes of polymers. A list of 314 references is included.

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I. INTRODUCTION

Determination of the molecular mass of a polymer is one of the most important problems in research on macromolecular compounds. Two "absolute" methods—light scattering and sedimentation–diffusion analysis of the polymer in solution—can usually be successfully applied[1]. However, neither method is effective with many polymers commonly used at the present time, which dissolve only in highly specific solvents[2]. The molecular masses of such polymers must therefore be found from certain hydrodynamic characteristics of their molecules, which can be determined experimentally with adequate reliability. Such characteristics are primarily the intrinsic viscosity $[\eta]$ and the coefficient of sliding friction of the molecule f, the latter determined from diffusion in solution.

II. CONCEPT OF THE HYDRODYNAMIC INVARIANT

Both intrinsic viscosity $[\eta]$ and coefficient of friction f are related to the molecular mass M or the contour length of the molecular chain $L = \lambda M/M_0$ (where λ is the projection of a monomer unit in the direction of the chain) by the well known formulae[1,3]

$$[\eta] = \Phi(LA)^{3/2}/M \qquad (1)$$

$$f = kT/D = P\eta_0(LA)^{1/2} \qquad (2)$$

in which D is the coefficient of translational diffusion of the polymer at infinite dilution, η_0 the viscosity of the solvent, A the Kuhn segment length representing the equilibrium rigidity of the polymer chain, M_0 the molecular mass of a monomer unit, k Boltzmann's constant, T is the temperature, and Φ and P are hydrodynamic coefficients depending on L, A, and certain other parameters such as intramolecular hydrodynamic interaction and effects of the excluded volume in non-ideal (non-θ) solvents. Calculation of the functions Φ and P is the main object of theories of the hydrodynamic properties of macromolecules in solution[3]. If the coefficient of friction f is determined experimentally not from diffusion but from sedimentation measurements, formula (2) is replaced by the equivalent expression

$$f = (M/sN_A)(1-\bar{v}\rho) = P\eta_0(LA)^{1/2} \qquad (3)$$

in which s is the sedimentation coefficient at infinite dilution, N_A Avogadro's number, $\bar{v}$ the specific partial volume of the polymer in solution, and ρ the density of the solvent.

Each of the relations (1)–(3) contains, in addition to one quantity that can be measured experimentally ($[\eta]$, D, or s), two molecular characteristics A and L (or $M = LM_0/\lambda$), which determine the equilibrium rigidity and the molecular mass respectively of the polymer chain. In order that the molecular mass can be found from experimental values of intrinsic viscosity or coefficient of friction, it is therefore necessary that both A and the form of function $\Phi(L, A)$ or $P(L, A)$ should be known for the given polymer. Since such data are usually absent for a newly investigated polymer, neither viscometry, measurement of diffusion coefficient, nor rapid sedimentation can usually serve in isolation as an independent method (not involving preliminary calibration) for determining the molecular mass of the polymer. However, use of two independently determined experimental quantities in Eqns.(1)–(3), with simultaneous solution of the appropriate pair of these equations, may yield an expression that does not contain the product LA in explicit form. Thus the two formulae (2) and (3) will give Svedberg's equation, from which are absent not only LA but also the parameters Φ and P and which serves as the chief absolute method for determining molecular mass from combined sedimentation and diffusion data.

Elimination of LA from formulae (1) and (2) yields the relation

$$kP^{-1}(\Phi/100)^{1/3} = \eta_0 D(M[\eta]/100)^{1/3}T \equiv A_0 \qquad (4)$$

while the use of Eqns.(1) and (3) for this purpose gives

$$kP^{-1}(\Phi/100)^{1/3} = R\eta_0(1-\bar{v}\rho)^{-1}M^{-2/3}([\eta]/100)^{1/3}s \equiv A_0 . \qquad (5)$$

The expression on the right-hand side of (4) was first discussed by Vallet[4,5], who measured diffusion coefficients and intrinsic viscosities for polystyrene fractions differing in molecular mass, and showed that the product $(M[\eta])^{1/3}D\eta_0$ was invariant in a series of these fractions. He explained this rule by regarding the polymer molecule as a solid sphere and applying to it the Stokes and Einstein laws to describe the diffusion and viscosity phenomena of polymer solutions. A little later Mandelkern and Flory[6] based the invariance of (5) on a chain molecule regarded as a hydrodynamically impermeable sphere of radius proportional to the mean square distance between the ends of the chain $\langle h^2\rangle^{1/2}$, with both P and Φ considered to be universal constants for all polymers.

At the same time Tsvetkov and Klenin[7], using the Debye–Bueche model of a partly permeable sphere[8], showed that the parameter A_0 (Eqn.4) can in principle be invariant over a

wide range of molecular masses even with appreciable permeability of the molecular coil, i.e. under conditions such that P and Φ do not individually remain constant with variation in molecular mass. They illustrated the invariance of A_0 by measuring D and $[\eta]$ of polystyrene fractions in dichloroethane over the molecular-weight range $(250-1320) \times 10^3$ g mole^{-1} and determining the corresponding value $A_0 = (3.42 \pm 0.06) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. From this they concluded[7] that it was possible and advisable to determine the molecular masses of polymers from viscosimetric data and the measured diffusion coefficient of their solutions by means of formula (4) and the above value of A_0.

In order to demonstrate the possibility of using this method it is necessary to analyse in greater detail the properties of the polymer–solvent system that ensure invariance of the hydrodynamic parameter A_0.

III. THEORY OF THE HYDRODYNAMIC PROPERTIES OF MACROMOLECULES

1. Chain Length and Hydrodynamic Interaction

If a solution is present under θ-conditions and the conformation of a molecular chain can be regarded as a Gaussian coil (i.e. $\langle h^2 \rangle = LA$), expressing P and Φ in formula (4) in terms of the theory of sliding friction and Kirkwood–Riseman viscosity[9] respectively yields for A_0 the expression

$$A_0 = \frac{k}{6\pi}(N_A/100)^{1/3} F(\sigma) \tag{6}$$

$$F(\sigma) = \frac{1+(8/3)\sigma}{\sigma}\left[\frac{\sigma}{1+(2/3)\sigma}\right]^{1/2} \tag{7}$$

in which

$$\sigma = \frac{3}{\sqrt{6\pi}} \cdot \frac{d}{\lambda}\left(\frac{L}{A}\right)^{1/2} \tag{8}$$

is a parameter representing the intramolecular hydrodynamic interaction. It follows from (6)–(8) that A_0 is a function of the relative chain length L/A, the length of a monomer unit λ in the direction of the chain, and its hydrodynamic diameter d (i.e. the diameter of a sphere representing a monomer unit for sliding friction).

For a polymeric homologous series (d/λ constant) the dependence of A_0 on chain length L can be readily ascertained by analysing the expressions (6)–(8). With increase in L/A and hence in the parameter σ the function $F(\sigma)$ tends to the limit $F(\sigma)_\infty = (8/3)(3/2)^{1/3} = 3.053$, while A_0 tends to $A_\infty = 4.1 \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$ (or 4.1×10^{-17} J deg^{-1} mole$^{-1/3}$). With very small L/A values and hence $\sigma \ll 3/8$, on the other hand, it follows from (7) that $F(\sigma) \approx \sigma^{-2/3}$ and $A_0 \to \infty$ as $L/A \to 0$, as noted previously[1]. Thus, according to theory[9], at sufficiently low values of L/A the parameter A_0 is by no means invariant but increases with decrease in chain length. Since, however, $d/\lambda \approx 1$, it is readily seen that this increase becomes appreciable only when $L/A < 1$: for example, with $L/A = 0.5$ the value of A_0 exceeds A_∞ by only 10%; throughout the remaining range of values $1 < L/A < \infty$, it follows from (6)–(8) that A_0 is indeed invariant, differing from A_∞ at most by tenths percent.

It must be borne in mind, however, that the hydrodynamic properties of polymer chains in the range $L/A \leq 1$ cannot be discussed in terms of a theory[9] that regards a polymer molecule as a Gaussian chain, which assumes that $L/A \gg 1$.

Hence theories of the hydrodynamic properties of vermiform chains must be used to discuss the dependence of A_0 on chain length throughout the range of possible values of L/A. The best hydrodynamic model of a chain molecule in a θ-solvent may be a vermiform cylinder of contour length L and diameter d, the ends of which are bounded by hemispheres[10,11].

With this model expressions have been obtained for the parameters P and Φ as functions of the relative length L/A and the relative diameter d/A of the chain molecule[10–13]. They can be written as the ratios P_∞/P and Φ/Φ_∞, where $P_\infty = 9/4(\pi/6)^{1/2}\pi = 5.11$ and $\Phi_\infty = 2.87 \times 10^{23}$ mole^{-1} are the asymptotic values of P and Φ as $L/A \to \infty$. In the range $L/A \geq 2.28$ we have[12]

$$\frac{P_\infty}{P} = 1 + \frac{B_2}{B_1}\left(\frac{L}{A}\right)^{-1/2} + \frac{B_3}{B_1}\left(\frac{L}{A}\right)^{-1} + \frac{B_4}{B_1}\left(\frac{L}{A}\right)^{-3/2} + \frac{B_5}{B_1}\left(\frac{L}{A}\right)^{-2} \tag{9}$$

where

$$B_1 = \frac{4}{3}\left(\frac{6}{\pi}\right)^{1/2} = 1.843;$$

$$B_2 = \left[-1-0.01412\left(\frac{d}{A}\right)^2 + 0.00592\left(\frac{d}{A}\right)^4\right]\ln\frac{d}{A} - 1.0561 - 0.1667\frac{d}{A} - 0.19\left(\frac{d}{A}\right)^2 - 0.0224\left(\frac{d}{A}\right)^3 + 0.019\left(\frac{d}{A}\right)^4;$$

$$B_3 = 0.1382 + 0.691\left(\frac{d}{A}\right)^2;$$

$$B_4 = -\left[0.04167\left(\frac{d}{A}\right)^2 + 0.00567\left(\frac{d}{A}\right)^4\right]\ln\frac{d}{A} - 0.3201 + 0.5\frac{d}{A} - 0.585\left(\frac{d}{A}\right)^2 - 0.0094\left(\frac{d}{A}\right)^3 - 0.0421\left(\frac{d}{A}\right)^4;$$

$$B_5 = -0.03 + 0.1209\left(\frac{d}{A}\right)^2 + 0.0259\left(\frac{d}{A}\right)^4.$$

The corresponding expression over the range $L/A \leq 2.28$ is[10]

$$\frac{P_\infty}{P} = \left(\frac{A}{L}\right)^{1/2} B_1^{-1}\left[C_1 \ln\frac{L}{d} + C_2 + C_3\frac{L}{A} + C_4\left(\frac{L}{A}\right)^2 + C_5\left(\frac{L}{A}\right)^3 + C_6\left(\frac{L}{A}\right)^4 + C_7\left(\frac{L}{A}\right)^5 + \ldots\right] \tag{10}$$

in which

$$C_1 = 1 - 0.125\frac{L}{d}\cdot\frac{d}{A} + 0.1406\frac{d}{L}\left(\frac{d}{A}\right)^3;$$

$$C_2 = 0.386 + 0.6863\left(\frac{d}{L}\right) - 0.0625\left(\frac{d}{L}\right)^2 - 0.01042\left(\frac{d}{L}\right)^3 - 0.000651\left(\frac{d}{L}\right)^4 + 0.0005859\left(\frac{d}{L}\right)^5;$$

$$C_3 = 0.1667 - 0.06838\left(\frac{d}{L}\right)^2 + 0.02083\left(\frac{d}{L}\right)^3 - 0.01693\left(\frac{d}{L}\right)^4 - 0.00859\left(\frac{d}{L}\right)^5;$$

$$C_4 = 0.01111 + 0.07917\left(\frac{d}{L}\right)^2 - 0.1799\left(\frac{d}{L}\right)^3 + 0.1055\left(\frac{d}{L}\right)^4 + 0.02461\left(\frac{d}{L}\right)^5;$$

$$C_5 = 0.001058 - 0.00496\left(\frac{d}{L}\right)^2 + 0.001653\left(\frac{d}{L}\right)^3 - 0.07348\left(\frac{d}{L}\right)^4 - 0.03281\left(\frac{d}{L}\right)^5;$$

$$C_6 = 0.0001587 - 0.0007275\left(\frac{d}{L}\right)^2 + 0.0003638\left(\frac{d}{L}\right)^3 - 0.0863\left(\frac{d}{L}\right)^4 + 0.4\left(\frac{d}{L}\right)^5;$$

$$C_7 = 0.00003748 - 0.0001714\left(\frac{d}{L}\right)^2 + 0.0001142\left(\frac{d}{L}\right)^3 + 0.006183\left(\frac{d}{L}\right)^4 - 0.002897\left(\frac{d}{L}\right)^5.$$

The function Φ/Φ_∞ with $LA \leq 2.28$ can be calculated[11] by means of the formula

$$\frac{\Phi}{\Phi_\infty} = \frac{\pi N_A}{24\Phi_\infty}\left(\frac{L}{A}\right)^{3/2} F(p)\cdot f\left(\frac{L}{A}\right) \tag{11}$$

in which $p = L/d$, $\Phi_\infty = 2.87 \times 10^{23}$ mole^{-1}, and

$$F(p) \equiv F\left(\frac{L}{A}, \frac{A}{d}\right) = \frac{16}{15}\left\{\ln p + 2\ln 2 - \right.$$
$$- \frac{25}{12} + \frac{\ln 2}{\ln(p+1)}\left[\frac{8}{75} - 2\ln 2 + \frac{25}{12} - 4.970572\right] + \frac{3.60517}{p^{1/4}} - \frac{15.35634}{p^{1/2}} +$$
$$\left. + \frac{28.0617}{p^{3/4}} - \frac{14.8934}{p} + \frac{3.553442}{p^{5/4}}\right\};$$

$$f(L/A) = 1 - 0.321593\frac{L}{A} - 0.0466384\left(\frac{L}{A}\right)^2 + 0.106466\left(\frac{L}{A}\right)^3 -$$
$$- 0.0379817\left(\frac{L}{A}\right)^4 + 0.00399576\left(\frac{L}{A}\right)^5 .$$

Values of Φ in Table 1 of Ref. 13 can be used to calculate Φ/Φ_∞ over the range $L/A \geq 2.28$.

Table 1. Values of A_0/A_∞ for various relative lengths L/A and relative diameters d/A of a vermiform chain.

L/A	A/d						
	2000	1000	200	100	100/3	100/6	10
10^6	0.998	0.999	0.999	0.999	0.999	0.999	1.000
10^5	0.995	0.996	0.996	0.997	0.997	0.998	0.999
10^4	0.997	0.998	0.990	0.990	0.991	0.994	0.996
10^3	0.976	0.978	0.978	0.978	0.978	0.983	0.989
500	0.977	0.977	0.975	0.974	0.973	0.978	0.985
200	0.989	0.985	0.976	0.972	0.967	0.971	0.978
100	1.008	1.000	0.982	0.975	0.965	0.965	0.971
70	1.024	1.013	0.989	0.979	0.965	0.962	0.967
50	1.043	1.029	0.997	0.985	0.967	0.960	0.962
20	1.115	1.090	1.033	1.011	0.977	0.956	0.948
10	1.186	1.151	1.070	1.037	0.987	0.953	0.934
7	1.225	1.184	1.090	1.051	0.991	0.951	0.926
5	1.261	1.215	1.108	1.052	0.992	0.948	0.917
2.278	1.339	1.282	1.144	1.084	0.990	0.934	0.897
2.0	1.362	1.300	1.154	1.092	0.995	0.938	0.899
1.0	1.382	1.312	1.149	1.079	0.973	0.910	0.868
0.6	1.380	1.306	1.133	1.060	0.950	0.886	0.844
0.4	1.362	1.286	1.109	1.035	0.923	0.861	0.821
0.2	1.310	1.231	1.051	0.977	0.870	0.813	0.778
0.1	1.242	1.162	0.983	0.912	0.816	0.768	0.758
0.05	1.167	1.088	0.914	0.850	0.768	—	—

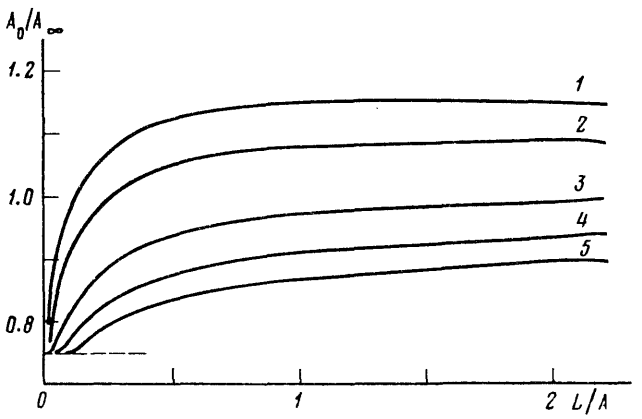


Figure 1. Dependence of A_0/A_∞ on relative length L/A of a vermiform chain in the range of low values $L/A = 0-2$ for different relative chain diameters d/A: *1*) 0.005; *2*) 0.01; *3*) 0.03; *4*) 0.06; *5*) 0.1.

Calculations based on Eqns. (9)–(11) enable the parameter $A_0 = kP^{-1}(\Phi/100)^{1/3}$ to be determined throughout the range of possible values of L/A and A/d. The results thus obtained for $A_0/A_\infty = (P_\infty/P)(\Phi/\Phi_\infty)^{1/3}$ are listed in Table 1 and illustrated by the curves in Figs. 1 and 2. The upper limit to A_0 predicted by theory[12,13] is $A_\infty = kP^{-1}(\Phi_\infty/100)^{1/3} = 3.84 \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. A finite limiting value of A_0 at low L/A is also predicted by theory[10,11], and is obtained from formulae (10) and (11) by putting $L/A = d/A \to 0$. We then find that $\lim_{L/A \to 0}(A_0/A_\infty)$ and $\lim_{L/A \to 0} A_0$ are respectively 0.75 and 2.88×10^{-10} erg deg^{-1} mole$^{-1/3}$.

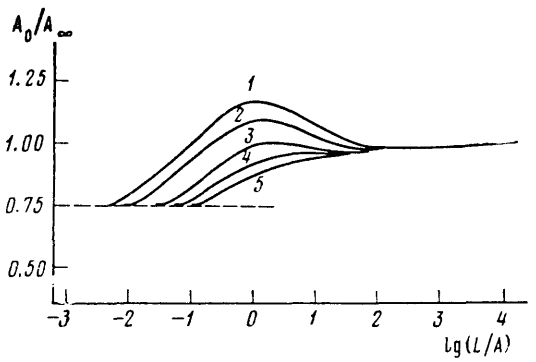


Figure 2. Dependence of A_0/A_∞ on L/A over a wide range for a vermiform chain having the same relative diameters d/A as in Fig. 1.

Table 1 together with Figs. 1 and 2 shows that according to theory[10,11] the parameter A_0 is invariant and close to A_∞ for all polymers in the range $L/A > 20$, where the molecule has a coiled conformation. With flexible-chain polymers ($d/A > 0.1$) in the range $L/A < 20$ a monotonic decrease in A_0 to its lower limit (i.e. by 25%) must be expected with decrease in chain length. In the case of polymers having moderately rigid chains ($0.1 \geq d/A \geq 0.03$) this decrease begins at lower values of L/A and is most developed in the range $L/A \leq 1$. Finally, the theory predicts for polymers of high equilibrium chain rigidity ($d/A \leq 0.01$) a non-monotonic dependence of A_0 on L/A in the region of short chains: A_0 increases with decrease in L in the range $L/A < 10$, reaches a maximum in the region of $L/A \approx 1$, and then drops abruptly to a lower limit. Thus in the region of short chains ($L/A \leq 10$), where A_0 can be expected to change with L/A, theory[10,11] indicates that a more rigid polymer has a rather higher value of A_0. This last conclusion is consistent with calculations[13] of A_0 for the range $L/A \geq 10$.

2. Excluded-volume Effects

If the conditions of a polymer solution are non-θ, osmotic swelling of the molecular coil may in principle influence not only P and Φ but also A_0, since change in molecular conformation in a thermodynamically "good" solvent is associated with change in intramolecular hydrodynamic interaction.

In the original form of Flory's theory of volume effects it was assumed that, on extension of a molecular coil in a "good" solvent and with increase in its linear dimensions (i.e. $\langle h^2 \rangle^{1/2}$) by a factor α, the coefficient of sliding

friction f also increases by this factor, while the intrinsic viscosity increases by a factor α^3. Hence P and Φ in formulae (1) and (2)—and thus also A_0 in (4)—were regarded as universal constants, remaining unchanged when a θ-solvent was replaced by a "good" solvent.

Later, however, it proved necessary to assume, in order to explain experimental results obtained for solutions of flexible-chain polymers, that linear extension of a molecular coil by a factor α was accompanied by change in f by a factor α_f, and in $[\eta]$ by a factor α_η^3, with both α_f and α_η smaller than α. Therefore the values of P and Φ in a "good" solvent should be less than their limiting values P_∞ and Φ_∞ in a θ-solvent, in conformity with the equations

$$P/P_\infty = \alpha_f/\alpha \; ; \; \Phi/\Phi_\infty = (\alpha_\eta/\alpha)^3 \; . \qquad (12)$$

Theories of volume effects in solutions of flexible-chain polymers and their influence on P and Φ were developed in a series of papers[3]. Although the results of different theories in several cases are by no means in quantitative agreement, they all lead to analogous qualitative conclusions: (i) both P and Φ diminish under the influence of volume effects; and (ii) increase in α produces a greater change in Φ than in P. For example, in an approximate calculation Kurata and Yamakawa obtained[3]

$$\Phi/\Phi_\infty = 1-0.46\,z+\ldots, \quad P/P_\infty = 1-0.22\,z \qquad (13)$$

where z is the excluded-volume parameter. Equation (13) yields the relation

$$A_0/A_\infty = (1-0{,}46\,z)^{3/2}/(1-0{,}22\,z) = 1+0.07\,z \qquad (14)$$

between A_0 in a "good" solvent and A_∞ in a θ-solvent. According to Ref.14 volume effects produce a slight increase in A_0. On the other hand, if results obtained by Fixman[15] ($\Phi/\Phi_\infty = 1-0.2z$) and by Stockmayer and Albrecht[16] ($P/P_\infty = 1-0.03z$) are used, the ratio $A_0/A_\infty = 1-0.04z$ is found, which predicts a slight decrease in A_0 under the influence of volume effects. In view of the above it is evident that, even if volume effects in solutions of flexible-chain polymers do lead to changes in A_0, such changes are so insignificant that they cannot be reliably predicted by existing theories.

Table 2. Theoretical values of Φ_∞ and corresponding values of A_∞ ($P_\infty = 5.11$).

$10^{-23}\Phi_\infty$, mole^{-1}	$10^{10}A_\infty$, erg deg^{-1} mole$^{1/3}$	Ref.	$10^{-23}\Phi_\infty$, mole^{-1}	$10^{10}A_\infty$, erg deg^{-1} mole$^{1/3}$	Ref.
3.62	4.1	[9]	2.68	3.75	[23]
3.37	4.0	[20]	2.76	3.79	[24]
2.87	3.83	[21]	2.19	3.51	[25]
2.84	3.82	[22]	2.51	3.43*	[26]

*$P_\infty = 5.99$.

It has been shown experimentally[17] and confirmed theoretically[18] that the influence of volume effects on molecular conformation is considerably weaker with polymers having molecular chains of enhanced rigidity than with flexible-chain polymers. In practice this means that even in "good" solvents the coefficient α in formula (12) is close to unity, and still more that α_η and α_f are close to α. It can thus be expected that for rigid-chain polymers the parameters P, Φ, and A_0 will be extremely insensitive to volume effects, although Hearst's theory[14] predicts some increase in A_0 with increase in the excluded volume.

3. Numerical Values of the Constants P_∞, Φ_∞, and A_∞

It follows from Eqn.(4) that the value of A_∞ predicted by theory depends on the theoretical values of P_∞ and Φ_∞. Both the latter were first calculated, in terms of the theories of sliding friction and Kirkwood–Riseman viscosity[9], by "pre-averaging" the Oseen hydrodynamic interaction tensor T_{ik} (i.e. by averaging T_{ik} over all chain conformations before using it to calculate f or $[\eta]$). To this approximation the value $P_\infty = 5.11$ was obtained, later refined to 5.2,[19] practically identical with the former value, which is usually employed in modern work.

Calculation of Φ_∞ involves several model concepts and mathematical approximations, depending on the character of which different authors have obtained different results (Table 2, first column). The calculated values show a chronological tendency to decrease, in some measure because in the later calculations the authors attempted to avoid pre-averaging T_{ik}, which always leads to rather lower values of Φ_∞. The lowest value $\Phi_\infty = 2.19 \times 10^{23}$ mole^{-1} was obtained by Hearst and Tagami[25], who differed from all tne other investigators in using as molecular model a vermiform instead of a Gaussian chain.

Values of A_∞ in the second column of Table 2 have been calculated by means of Eqn.(4) from the corresponding value of Φ_∞ and $P_\infty = 5.11$ (apart from the last line, in which it is assumed that $P_\infty = 5.99$).

Values in the last line in Table 2 were obtained by Zimm[26], who made a thorough review of the effect of pre-averaging the hydrodynamic interaction in chain molecules on the calculation of coefficient of friction and intrinsic viscosity. Using the Monte Carlo method and generating in a computer experiment a set of random configurations of the polymer chain, he solved the problem of hydrodynamic interactions in sedimentation and viscosity phenomena for each configuration, and only then averaged the results. The values of Φ_∞, P_∞, and A_∞ thus obtained, extrapolated to a chain having an infinite number of segments, are included in Table 2. The values of Φ_∞ and A_∞ proved to be smaller, but those of P_∞ were larger, than the values usually employed. The value $P_\infty = 5.99$ appears most unusual, but it is noteworthy that at one time Kuhn et al.[27] obtained the still higher value $P_\infty = 7.3$ from experiments with wire models.

The above values of P_∞, Φ_∞, and A_∞ apply to a polymer that is homogeneous with respect to molecular mass. The presence of molecular-mass polydispersity in a specimen may be expected to lead to a decrease in Φ.[28] The parameter A_∞ also depends on polydispersity, and may be either diminished or increased depending on the way in which the experimental quantities D, s, $[\eta]$, and M in Eqns.(4) and (5) have been averaged[29,30]. However, the variations in A_∞ to be expected in moderately polydisperse specimens are small[29], and in many cases can apparently be disregarded.

IV. EXPERIMENTAL RESULTS

1. Values of Φ and P

It follows from Eqns.(1)–(3) that experimental determination of the coefficient Φ or P separately requires the measurement of two or three molecular characteristics. One of these must necessarily be the radius of inertia of the chain molecule, which for a polymer of sufficiently high molecular mass in a θ-solvent is $\langle R\rangle = (LA/6)^{1/2}$. Measurement of this radius, which is based on the asymmetry of light scattering, is a most difficult experimental procedure, always entailing the possibility of considerable errors and

inaccuracies. Incidentally, the method of light scattering permits determination of a second quantity—the molecular mass M—occurring in Eqns.(1) and (3). Finally, the third quantity which must be measured experimentally is either the intrinsic viscosity (for the determination of Φ by means of Eqn.1) or the sedimentation coefficient s (if P is determined from formula 3). When the latter is determined by means of (2), it is necessary to measure the diffusion coefficient D in addition to the radius of inertia, but the molecular mass is not required in this case.

Table 3. Experimental values of the coefficient Φ for polystyrene in a θ-solvent (cyclohexane) at 35 °C.

$10^{-6} M_w$, g mole^{-1}	$10^{-23} \Phi$, mole^{-1}	Ref.
3.2	1.85	31
4.0	1.76	32
0.62—1.6	2.6—2.9	33
0.62—4.4	1.7—2.6 *	33
0.21—1.0	1.8—2.4	34
0.34—2.9	2.4—2.6	35
27—44	1.5—2.0	36
1.2—4.6	2.2—2.8 *	37
8.8—57	2.2—2.4	38, 39
6.5	2.5±0.1	40
0.21—1.0	2.4—1.98 **	34

*In decalin (θ-solvent) at 20.4 °C.
**In cyclohexene ("good" solvent) at 25 °C.

Since viscometry is a considerably more accessible procedure than measurement of sedimentation or diffusion coefficients, the majority of the experimental work has involved the determination of Φ by means of formula (1). In most cases polystyrene having a narrow molecular-mass distribution was used in a θ-solvent. Table 3 gives several typical results of such measurements. The experimental values show a considerable scatter. However, they do indicate that, despite the quite high molecular masses of the test specimens, the values obtained for Φ were usually considerably lower than the theoretically predicted Φ_∞ values (Table 2). An unambiguous dependence of Φ on the nature of the solvent cannot be discerned from existing results[34].

Table 4. Experimental values of the coefficients P for several polymer–solvent systems (under θ-conditions).

Polymer	Solvent	Temp., °C	P	Ref.
Polystyrene	butan-2-one–n-butanol	25	4.7	41
Poly(methyl methacrylate)	1-chlorobutane	35	6.3	42
Polystyrene	cyclohexane	35	5.3	34
Polystyrene	cyclohexane*	25	5.7	34
Poly-α-methylstyrene	cyclohexane	34.5	5.5	43, 44

*Thermodynamically "good" solvent.

Published information on the experimental determination of P is extremely meagre, practically limited to the examples in Table 4. Four of the five experimental values of P exceed the 5.11 predicted by theory, and only one is lower. The difference between values of P for polystyrene in a "good" solvent and in a θ-solvent could be attributed[34] equally to an excluded-volume effect and to scatter due to experimental error. Thus the problem of reliable experimental values of Φ and P remains open, and requires further careful investigation.

Comparison of the experimental results in Tables 3 and 4 with the theoretical values in Table 2 indicates that Zimm's method[26], using the technique of a computer experiment and avoiding pre-averaging of the Ozeen tensor, gives better agreement between theoretical and experimental values of Φ and P than that obtained by other workers. In view of the great scatter and unreliability of available experimental results and also the difficulties of theoretical calculations, however, it seems premature to adopt Zimm's values as the most reliable and the preferred for use.

2. Values of A_0

Discrepancies in the experimental values of Φ and P obtained by different authors are due not only to polydispersity of the specimens (to which reference has often been made) but primarily and in no less degree to errors in the measurements of molecular dimensions $\langle h^2 \rangle$ or $\langle R^2 \rangle$ from the asymmetry of light scattering in solutions of the polymer. As already mentioned, calculation of A_0 from experimental results requires values of molecular mass, intrinsic viscosity, and coefficient of friction, while the procedure involved in determining $\langle R^2 \rangle$ is excluded. Therefore the accuracy and the reliability of the experimental determination of A_0 in principle exceeds considerably those of the determination of Φ and P.

If molecular mass is determined from the scattering of light (in which method asymmetry indicatrixes, though used, play a considerably less important part than in the measurements of $\langle R^2 \rangle$), the calculation of A_0 requires the determination of coefficient of friction in addition to the measurement of intrinsic viscosity. Such determination can be made by rapid sedimentation and A_0 calculated by means of formula (5); or diffusion measurements can be used for this purpose, and A_0 calculated by means of (4). In the latter method the accuracy with which the diffusion coefficient is measured becomes important, since in Eqn.(4) it is raised to a power thrice that of molecular mass and intrinsic viscosity.

If molecular weight is determined by a combination of the diffusion and rapid sedimentation methods, replacing M by M_{sD} in formula (4) or (5) with use of the Svedberg equation yields

$$A_0 = \eta_0 \left(\frac{D}{T}\right)^{2/3} \left(\frac{[\eta] sR}{100(1-\bar{v}\rho)}\right)^{1/3}. \qquad (15)$$

Thus in this case the determination of A_0 involves in effect sedimentation–diffusion and viscosimetric measurements, in which as before the accuracy with which diffusion coefficient is determined is important, since in (15) the power to which this factor is raised is double that of the sedimentation coefficient and the intrinsic viscosity.

A comparative assessment of the suitability of the different methods for determining A_0 must first take into account the experimental difficulties associated with the use of light scattering, which requires that the test solutions be highly purified. This applies especially to those cases in which sparingly soluble polymers are investigated in binary solvents, polyelectrolyte buffer solutions, and other such systems that are difficult to purify.

The sedimentation and diffusion methods do not require such careful purification of the solution, which is a substantial advantage in comparison with the light-scattering method. When aqueous and buffer solvents are

used, however, a complication arises from charge effects when diffusion and sedimentation coefficients are measured in polyelectrolyte systems. Although these effects may be diminished by increasing the ionic strength of the solution and reliably extrapolating to zero polymer concentration[45] using a sensitive interferometric technique[1], their complete elimination is difficult to guarantee. Furthermore, a significant error in the sedimentation method is associated with measurement of the partial specific volume $\bar{v}$, which governs the buoyancy factor $1-\bar{v}\rho$ in Eqns.(5) and (15). This disadvantage is absent in the diffusion method, which does not require measurement of the partial specific volume and enables the coefficient of friction f to be determined most directly.

Table 5. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for fractions of flexible-chain polymers in thermodynamically "good" solvents.

Polymer (M_w/M_n)	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0$*	Type of M; methods	Ref.
Rubber, natural	125—515	chloroform	20	3.51±0.20	M_n; S, D, LS, OS	[46]
»	1600	cyclohexane	20	3.26	M_{SD}; S, D,	[47]
Polyacrylonitrile	48—270	dimethylformamide	25	3.52±0.04	M_{SD}; S, D	[48]
», $M_w/M_n=1.69$	105	" (deionised)	25	3.40	M_w; S, LS, OS	[49]
», $M_w/M_n=2.04$	210	»	25	3.01	M_w; S, LS, OS	[49]
cis-Polybuta-1,4-diene (≤1.1)	50—1100	heptane - hexane (1 : 1)	20	3.15	M_{SD}; S, D	[50, 51]
Poly(vinyl acetate) (1.44)	17—1200	butan-2-one	25	3.04±0.46	M_{SD}; S, D, LS, OS	[52, 53]
Poly-2-vinylnaphthalene	72—1230	benzene	20	3.15±0.09	M_{SD}; S, D	[54]
»	3500	tetrachloromethane	20	3.50	M_{SD}; S, D	[54]
Polyvinyldimethylpropylsilane (1.5 - 2.0)	62—306	cyclohexane	25	3.39±0.24	M_w; S, D, LS	[55]
»	62—306	»	25	(2.56)	M_{SD}; S, D	[55]
Poly-4-vinylpyridine	11.6—847	chloroform	21	2.75±0.24	M_{SD}; S, D	[56]
Polyvinylpyrrolidone	10.6—86	water	20	3.25±0.24	M_{SD}; S, D	[57]
»	13.3—42.1	water	20	3.32±0.10	M_{SD}; S, D	[58]
Poly(vinyl stearate)	62—840	n-octane	18	3.19±0.12	M_{SD}; S, D, LS	[59]
Poly(vinyl chloride)	53, 120	oxolan	25	2.96±0.13	M_w; S, LS	[30]
Poly(vinyl cinnamate)	51—762	butan-2-one	22	3.58±0.10	M_{SD}; S, D	[60]
Polydimethylsiloxane (1.2)	101—550	bromocyclohexane	28	1.90±0.14	M_{SD}; S, D, LS	[61]
»	301—920	toluene	20	3.68±0.21	M_{SD}; S, D, LS	[61]
»	76—2360	tetrachloromethane	24	3.02±0.24	M_w, M_η; D, LS	[62]
Poly-(2,6-dimethyl-1,4-phenylene ether) (M_z/M_w 1.2)	87	toluene	25	2.56	M_w; S, LS, SE	[63]
»	87	tetrachloroethane	25	2.33	M_w; S, LS, SE	[63]
Polyisobutylene (≥2)	9.7—308	n-heptane	25	3.46±0.25	M_w; D, LS	[64]
»	0.6—35	di-isobutylene	—	3.0	—	[65]
»	31—1420	cyclohexane	20	3.48±0.14	M_n; S, OS	[66]
»	0.6—35	cyclohexane - decalin	—	3.2	—	[65]
», «L-80»	800	ethyl octanoate	22	4.23	M_η; D	[67]
cis-1,4-Polyisoprene (≤1.1)	50—1000	hexane - propan-2-ol (1 : 1)	21	3.01	M_{SD}; S, D	[51]
Poly-2-methyl-5-vinylpyridine	120—1110	chloroform	21	3.34±0.08	M_{SD}; S, D	[56]
»	100—2590	ethyl acetate	25	3.16±0.20	M_{SD}; S, D	[68]
Polymethylene (2.04 ± 0.34)	4.6—58	1-bromonaphthalene	110	3.41±0.13	$(M_w)_\eta$; S	[69]
Poly-α-methylstyrene (1.00 ± 0.03)	44.4—1675	benzene	30	3.19±0.13	M_w; S, LS, OS	[70]
», (0.95-1.11)	67.6 - 1170	toluene	25	**3.27±0.12	M_w; S, LS	[71]
», "monodisperse"	204—7470	toluene	25	**3.18±0.10	M_w; S, LS	[43]
»	1190—7470	*trans*-decalin	20	**3.35±0.08	M_w; S, LS	[43]
»	204—7470	»	40	**3.22±0.05	M_w; S, LS	[43]
Polynonyloxybenzamidostyrene	37	benzene	21	3.13	M_{SD};S, D	[72]
Polyoxypropylene glycol	0.85—2.64	chloroform	24	3.24±0.25	M_n; D, OS	[73]
Poly(propylene sulphide)	37—208	benzene	21	3.24±0.11	M_{SD};S, D, LS	[74]
Polystyrene	1.18—520	»	—	3.12±0.21	M_{SD};S, D	[75]
», (M_z/M_w ≤ 1.2)	3600	»	40	**3.17	M_w; S, LS	[32]
»	4.5—85	»	—	2.6	M_w; D, LS	[65]
», "BASF IIID" (M_z/M_w ~1.9)	220	»	25, 30, 35	3.0±0.1	M_{SD};S, D	[76]
»	1000	*trans*-decalin	25	3.19	M_w; D	[77]
Pressure Chemical Co., "lot N14a" (~1.2)	1800	»	25	3.07	—	[78]
», (M_{SD}/M_n 1.06)	420	»	20, 30, 40	3.00±0.09	M_{SD};S, D, OS	[79]
»	250—1320	dichloroethane	—	3.52±0.06	M_w; D, LS	[7]
»	130	3-methylbutan-2-one	20	3.29	—	[5]
»	180—270	butan-2-one	20	2.65—2.85	M_n; D, OS	[4]
»	254—1240	»	20	3.58±0.08	M_η	[80, 6]
»	1000	»	25	3.44	M_w; D	[77]
», (1.44)	114—955	»	20	3.20±0.28	M_w; S, LS, OS	[81]
», "IUPAC 11-26-52" (1.17; M_z/M_w 1.24)	538±75	»	20	3.4±0.1	M_w; S, LS, OS	[82]
»	325—2800	»	25	**3.44±0.18	M_w; S, LS	[41]
»	540	»	20	3.39	M_w; S, D, LS	[83]
», "S102, S111, KL-4" (1.15 ± 0.09)	85—415	»	25	2.81±0.06	M_w; S, LS, OS	[84] [85]
», (~1.06)	51—110	oxolan	30	2.99±0.10	M_w; D_z, LS	[86]
»	51—110	»	30	3.2	M_w; D_z, LS	[86]
»	1000	tetrachloromethane	25	4.23	M_w; D	[77]
»	45—700	»	24	3.42	M_w; D, LS;	[87]
»	130	toluene	20	3.27	—	[5]
»	180	»	20	3.04	—	[4]
»	180	»	20	3.72	—	[88]
»	270	»	20	2.91	—	[4]
»	254—1240	»	20	3.19±0.40	M_η; S	[80, 6]
»	1000	»	25	2.96	M_w;D	[77]
»	510—1920	»	25	3.94±0.12	M_η; D	[89]
»	535	»	25	3.24	M_{SD}; S, D	[90]
», "IUPAC 11-26-52" (1.17; M_z/M_w1.24)	538±75	»	20	3.3±0.2	M_w; S, LS	[82]
»	540	»	20	3.62	M_w; S, D, LS	[83]

Table 5 (cont'd.).

Polymer (M_W/M_η)	10^{-3} M	Solvent	Temp., °C	10^{10} A_2*	Type of M; methods	Ref.
», (≤1.2)	44—2800	»	20	3.35±0.17	M_{sD}; S, D	[91]
», "P-30"	75	»	23.5	2.82	M_w; S, LS	[67]
»	930—21000	»	21	2.1±0.4	M_w; S, LS	[92]
», (3 ± 1)	250—411	»	25	2.83±0.10	M_w; D_z, LS	[85]
Pressure Chemical Co., "lot NN 4b, 3b, 14a"	110—1800	toluene	25	3.07±0.10	—	[78]
», (M_{sD}/M_n 1.02)	112	»	25	3.12±0.09	M_{sD}; S, D, OS	[79]
», (1.2)	23 400—40 000	»	20	3.14±0.05	M_w; S, D, LS	[93, 94]
», (M_z/M_W 1.19)	118	»	25	**3.13	M_w; S, LS, SE	[63]
»	180	toluene–butanol (9:1, 8:2, 7:3)	(20)	3.01—2.30	M_n; D, OS	[88]
»	540	toluene–butan-2-one (1:1, 1:3, 3:1)	20	**3.51—3.43	M_w; S, D, LS	[83]
»	540	chloroform	20	**3.50	M_w; S, D, LS	[83]
»	115—2800	»	25	**2.94±0.06	M_w; S, LS	[41]
», (M_z/M_W ≤1.2)	3600	cyclohexane	45, 55	**2.95; 3.10	M_w; S, LS, SE	[32]
»	130	cyclohexanone	20	3.44	—	[5]
», (1.02–1.14)	199—1064	cyclohexene	25	**3.15±0.10	M_w; S, D, LS	[34]
», "S102, S111, KL-4", (1.15 ± 0.09)	85—415	ethyl acetate	25	2.84±0.05	M_w; S, LS, OS	[84]
»	1000	ethylbenzene	25	2.53	M_w; D	[77]
Polystyrene latex	5870	0.098M NaCl	25	3.04	M_w; S	[95]
Polyepichlorohydrin (≤1.3)	28.9—168.4	oxolan	20	2.65±0.19	M_w; S, LS	[96]
Polyethylene, high density (1.55 ± 0.43)	3.8—245	1-bromonaphthalene	110	3.25±0.33	$(M_w)_\eta$, S	[69]
»	8—250	»	110	3.14	M_w; S, LS	[97]
Poly(ethylene oxide)	—	water	30	2.55	M_w; S, LS	[98]
(M_{sD}/M_n < 1.1)	320	»	25	2.88	M_{sD}; S, D	[99]
Poly(ethylene terephthalate) (M_{sD}/M_n 1.08 ± 0.09)	23—111.6	*m*-cresol	25	3.43±0.38	M_{sD}; S, D, OS	[100]
Polymers with a comb-like macromolecular structure, acrylates, and methacrylates						
Polyacrylamide (2.5)	770—5270	0.5M NaCl	20	2.76±0.26	M_w; S, LS, OS	[101]
», (1.2–1.4)	130—6700	water	20	3.38±0.48	M_w; S, LS	[102]
Poly-*p*-acryloylazoxybenzene	10—199	tetrachloroethane	27	3.29±0.31	M_{sD}; S, D	[103]
Poly(butyl acrylate)	40—940	butan-2-one	25	3.95±0.30	M_{sD}; S, D	[104]
Poly-n-butyl-*p*-acryloylazoxybenzene	26—78	tetrachloroethane	27	3.22±0.16	M_{sD}; S, D	[103]
Poly-(t-butyl crotonate), atactic (1.11–1.26)	60.6, 161	1-chlorobutane	25	3.75±0.02	M_w; D, LS, OS	[105]
»	60.6, 161	»	25	(3.54±0.10)	M_n; D, OS	[105]
Poly(butyl methacrylate)	34—148	butan-2-one	24	2.96±0.12	M_{sD}; S, D	[106]
»	40—8200	chloroform	24	**3.10±0.24	M_w; D, LS	[107]
poly-(*p*-t-butylphenyl methacrylate) (1.3)	42—1125	butan-2-one	25	2.97±0.10	M_w; S, LS	[108]
»	60—3650	chloroform	24	3.13±0.16	M_w; D, LS	[7, 109, 110]
Poly(vinyl laurate)	24—3000	heptane	25	3.31±0.18	M_{sD}; S, D	[111]
Poly(heptafluoromethoxyethylethylene oxide), isotactic (≤1.2)	450—1970	hexafluorobenzene	20	3.46±0.03	M_w; S, LS	[112]
»	833—1970	chloropentafluorobenzene	20	2.25±0.28	M_w; S, LS	[112]
»	573—952	hexafluorobenzene	20	3.46±0.05	M_w; S, LS	[112]
»	»	chloropentafluorobenzene	20	2.39±0.31	M_w; S, LS	[112]
Poly(decyl acrylate) (M_z/M_W 1.26 ± 0.09)	63—1110	heptane	24	**3.63±0.27	M_{sD}; S, D	[113]
Poly(decyl methacrylate)	42.5—4950	heptane	21	3.37±0.11	M_{sD} S, D	[114]
Poly-*p*-ethoxycarbonylphenylmethyacrylamide	180—1080	ethyl acetate	20	3.36±0.50	M_w; S, D, LS	[115]
Poly-(*p*-menth-5-yl methacrylate) 1.5)	125—2290	benzene	25	2.90±0.13	M_w; S, LS	[108]
Poly(methyl *p*-methacryloyloxy-benzoate)	180—4000	butyl acetate	24	3.25±0.05	M_{sD}; S, D	[116]
Poly(methyl acrylate)	70—2900	butan-2-one	25	3.26±0.24	M_{sD}; S, D	[104]
Poly(methyl methacrylate) (M_{sD}/M_n 1.16–1.46)	24.6—7440	acetone	20	3.29±0.16	M_{sD}; S, D, OS	[117—119]
»	24.6—7440	»	20	3.25±0.15	M_{sD}; S, D, LS	[120]
»	145—7600	»	20	3.33±0.18	M_w; S, D, LS	[120]
»	200—6550	»	20	**2.98±0.05	M_{sD}; S, D	[42]
»	200—6550	dioxan	25	**3.18±0.10	M_{sD}; S, D	[42]
»	70—4320	chloroform	24	3.19±0.15	M_w; D, LS	[7, 109, 110]
»	79—931	ethyl acetate	20	3.59±0.19	M_{sD}; S, D	[121]
»	64—1168	»	20	3.38±0.13	M_{sD}; S, D	[122]
», (M_z/M_W 1.7)	23 700	»	23	3.73	M_{sD}; S, D	[76]
», branched	769—2140	»	20	3.76±0.12	M_{sD}; S, D	[122]
», (1.48 ± 0.06)	162, 296	»	20	3.12±0.04	M_w; S, LS, OS	[123]
», branched*** (1.74 ± 0.05; n_W 0.26)	195, 396	»	20	2.75	M_w; S, LS, OS	[123]
», (M_z/M_W 2.36 ± 0.43; n_W 1.02)	301—620	»	20	2.14	M_w; S, LS, OS	[123]
», (10.1; n_W 7.25)	1340	»	20	(0.89)	M_w; S, LS, OS	[123]
Poly-(2-hydroxyethyl phthalimidomethacrylate)	770—20000	dimethylformamide	20	3.12±0.09	M_{sD}; S, D	[124]
Poly(octadecyl acrylate)	180—3590	heptane	25	3.00±0.10	M_{sD}; S, D	[104]
Poly(octyl acrylate)	120—3100	»	25	3.05±0.23	M_{sD}; S, D	[104]
Poly(octyl methacrylate)	150—2450	»	25	2.97±0.11	M_{sD}; S, D	[106]
Poly-(*p*-n-nonyloxyphenyl *p*-methacryloyl-oxybenzoate)	119—1700	benzene	24	3.28±0.14	M_{sD}; S, D	[125]
Polystyrene, comb-shaped (10)	90—190	»	25	3±1	M_n; S, D	[126]
»	440—1840	»	25	(6±2)	M_{sD}; S, D	[126]
Poly-(2-triphenylmethoxyethyl methacrylate) (M_z/M_W 1.16 ± 0.07) (≤1.2)	68—5200	»	26	2.85±0.13	M_{sD}; S, D	[127]
	51—2630	toluene	25	3.16±0.11	M_w; S, LS	[128]
Poly(phenyl methacrylate) (M_z/M_W 1.4 ± 0.2) (1.81 ± 0.16)	23—1100	butyl acetate	24	3.49±0.20	M_{sD}; S, D	[129]
	740—4970	butan-2-one	25	3.08±0.10	M_w; S, LS, OS	[130]
Poly(phenylmethacrylyl nonyloxy-benzoate)	200—2200	tetrachloromethane	25	3.26±0.16	M_{sD}; S, D	[131]
Poly(phenylmethacrylyl hexadecyloxy-benzoate)	1900	benzene	25	3.74	M_{sD}; S, D	[132]
»	1900	oxolan	25	2.80	M_{sD}; S, D	[132]
»	1900	tetrachloromethane	25	2.90	M_{sD}; S, D	[132]
»	146—20000	»	25	3.19±0.28	M_{sD}; S, D	[131]
Poly-(*p*-chlorophenyl methacrylate) (1.54 ± 0.07)	105—5630	benzene	25	3.93±0.09	M_w; S, LS, OS	[133]
Poly(cholesteryl acrylate)	140—780	»	21	3.07±0.24	M_{sD}; S, D	[134]
Poly(hexadecyl acrylate) (M_z/M_W 1.2–1.4)	47—140000	heptane	25	3.44±0.24	M_{sD}; S, D	[135]
Poly(hexadecyl vinyl ether)	3—30	»	25	3.13±0.10	M_{sD}; S, D	[136]
Poly(hexadecyl methacrylate) (M_z/M_W 1.22 ± 0.08)	1370—12600	»	25	3.23±0.21	M_{sD}; S, D	[137, 138]
»	220—2540	»	25	3.48±0.14	M_{sD}; S, D	[106]

Table 5 (cont'd.).

Polymer (M_W/M_η)	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0$*	Type of M; methods	Ref.
Poly(cylohexyl methacrylate) (1.11 ± 0.07)	170—4190	butan-2-one	25	3.21±0.20	M_w; S, LS, OS	[130]
»	170—1960	cyclohexane	25	3.26±0.17	M_w; S, LS, OS	[130]
Poly-(1*H*, 1*H*, 5*H*-octafluoro-n-pentyl methacrylate) (≤1.15)	2100—35700	»	21	3.36±0.09	M_{sD}; S, D	[139]
Poly-(1*H*, 1*H*, 7*H*-dodecafluoro-n-heptyl methacrylate) (≤1.15)	450—12400	»	21	3.03±0.12	M_{sD}; S, D	[139]
Poly(hexadecyl *p*-methacryloyloxybenzoate)	16—500	tetrachloromethane	25	3.29±0.38	M_{sD}; S, D	[140]
		Copolymers				
Butadiene-acrylonitrile, random 74:26	50—1300	butan-2-one-cyclohexane 36:64	20	2.98	M_{sD}; S, D	[51]
», 60:40	30—800	», 47.5:52.5	22	2.89	M_{sD}; S, D	[51]
», 82:20 (1.1-1.3)	35—291	butan-2-one-propan-2-ol 59:41	20	2.85±0.14	M_{sD}; S, D	[141]
», 46:54 (1.1-1.3)	17—162	butan-2-one-cyclohexane 74:26	21	2.79±0.10	M_{sD}; S, D	[141]
Butyl-hexadecyl methacrylate, random 1:1	220—920	heptane	25	3.22±0.04	M_{sD}; S, D	[106]
Vinyl acetate-vinylcaprolactam (6-10%), random	100—190	acetone	22	2.73±0.20	M_{sD}; S, D	[142]
1,1-Difluoroethylene-tetrafluoroethylene random (M_{SD}/M_η 1.2-1.6)	6—1250	dimethyl sulphoxide	25	4.0±0.20	M_{sD}; S, D	[143]
(M_{SD}/M_η 1.7-4.5)		»	25	(4.6±0.42)	M_{sD}; S, D	[143]
N-Vinylpyrrolidone-crotonic acid, random	34	0.2 M $NaNO_3$ in DMF	20	3.58±0.02	M_{sD}; S, D	[144]
Octyl-hexadecyl methacrylate, random 1:1	130—450	heptane	25	2.94±0.03	M_{sD}; S, D	[106]
Polystyrene-poly(methyl methacrylate) graft 0.9:0.1	600—7600	butyl acetate	25	2.62±0.33	M_{sD}; S, D	[145]
»	600—7600	chloroform	25	2.50±0.52	M_{sD}; S, D	[145]
» 0.87:0.13 (1.2)	775, 1310	butyl acetate	21	3.11±0.10	M_{sD}; S, D	[146]
» 0.875:0.125 (M_Z/M_W 1.08-1.17)	80—697	»	21	3.15±0.09	M_{sD}; S, D	[147]
Styrene-butadiene, random 27:75	40—800	octane	21	3.26	M_{sD}; S, D	[51]
Styrene-*p*-divinyltetrachlorobenzene (branched polystyrene) n(1.15% Cl), random (1.16 ± 0.09, internodal M 95 000)	47—1550	cyclohexane	35	3.51±0.12	M_w; S, LS, OS	[148]
Styrene-methacrylic acid		oxolan	—	3.1	—	[149]
Phenylmethacrylyl hexadecyloxybenzoate-hexadecyl methacrylate (6.5-88%)	1590—3460	tetrachloromethane	25	3.30±0.42	M_{sD}; S, D	[150]
», 1:1	700—120000	»	25	3.08±0.03	M_{sD}; S, D	[151]
», 7:3	320—11300	»	25	3.87+0.02	M_{sD}; S, D	[151]

*Values of A_0 in parentheses in Tables 5—10 disregarded in calculation of mean experimental values of A_0.

**These fractions investigated both in a thermodynamically "good" solvent (in this Table) and in a θ-solvent (Table 6).

***Here and subsequently n_W is the number of branchings per molecule.

From the above considerations it may be expected that the combination of light-scattering and sedimentation methods using formula (5) will lead to the greatest errors in the determination of A_0. On the other hand, the combination of diffusion and sedimentation methods involves formula (15), in which the buoyancy factor occurs as the cube root, which diminishes errors in the determination of partial specific volume, while the diffusion coefficient, occurring to the two-thirds power in (15), is measured quite reliably (by an interferometric technique[1]). Therefore the sedimentation–diffusion method for determining A_0 must be the most strongly preferred, at least when organic solvents are used.

Tables 5—10 list experimental values of A_0 for various polymer–solvent systems obtained by different methods in various laboratories. The methods used are indicated in the appropriate column by the abbreviations D for diffusion, S sedimentation, SE sedimentation equilibrium, LS light scattering, and OS osmometry. The type of averaging of molecular mass (M_W, M_n, M_{SD}) used in the calculation of A_0 is also indicated. In all cases viscometry was used in addition to the methods listed.

Table 5 lists numerous results obtained for flexible-chain (mainly vinyl) polymers in good (non-θ) solvents. All measurements were made on fractions of molecular-mass range indicated in the first column. Examination of original sources (from literature references) does not usually reveal any systematic variation in A_0 for individual fractions with their molecular weight. Table 5 gives values of A_0 averaged over all fractions of a given polymer in each paper, while the error indicated is a mean of the deviations from this value for different fractions. On comparing values of A_0 for the 172 different polymer–solvent systems (including ~800 fractions) represented in Table 5, it is impossible to detect any systematic dependence of A_0 on the method used.

The average of all values of A_0 in Table 5 is $(3.2 \pm 0.2) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. This mean scatter of values obtained by different authors in different polymer–solvent systems has the same order of magnitude as the scatter of A_0 values between different fractions of a polymer investigated in the same work, which gives grounds for supposing that differences in the values for different polymers lie within the limits of experimental error.

Table 6. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for flexible-chain polymers in θ-solvents.

Polymer	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0^*$	Type of M; methods	Ref.
Poly(butyl methacrylate)	40—8200	propan-2-ol	21.5	**3.44±0.20	M_n; D, LS	[107]
Poly(decyl acrylate) (M_z/M_w 1.26 ± 0.09)	63—1110	n-butanol	24.5	**3.60±0.28	M_{SD}; S, D	[113]
»	63—1110	ethyl acetate	10	**3.10±0.20	M_{SD}; S, D	[113]
Polydivinylstyrene	65—710	n-octane	21	3.20±0.10	M_{SD}; S, D	[152]
Polyisobutylene	1170	ethyl octanoate	10.8	3.53	M_{η}; S	[153]
Poly(methyl methacrylate)	200—6550	1-chlorobutane	35.6	**3.09±0.03	M_{SD}; S, D	[42]
	391	tetrachloromethane	15	3.55	M_{η}; S	[153]
Poly-α-methylstyrene, monodisperse	204—7470	*trans*-decalin	9.5	**3.37±0.07	M_w; S, LS	[43]
»	204—7470	»	»	(3.41)	M_w; S, LS	[154]
» (M_w/M_n 0.95–1.11)	42.5—1170	cyclohexane	39	**3.53±0.13	M_w; S, LS	[71]
» monodisperse	44.4—1675	»	39	3.27±0.08	M_w; S, LS, OS	[155]
» (M_w/M_n 1.03)	49—268	»	38.2	3.23±0.07	M_w; S, LS	[156]
» monodisperse	204—7470	»	34.5	**3.21±0.10	M_w; S, LS	[43]
» ($M_z/M_w \leqslant 1.2$)	120—2900	»	32	3.15±0.10	M_{SD}; S, D	[157]
Polystyrene	830—2300	butan-2-one–butan-1-ol 72:26	25	**3.38±0.12	M_w; S, LS	[41]
»	31.5—1500	cyclohexane	35	3.01±0.13	M_w; S, D, LS	[158]
»	530	»	35	**3.10	M_w; S, D, LS	[83]
» ($M_z/M_w \leqslant 1.2$)	3600	»	35	**2.98	M_w; S, LS	[32]
» (M_w/M_n 1.09)	85—3950	»	35	2.79±0.14	M_w; S	[159]
»	27—495	»	35	3.28±0.11	M_w; S, LS	[160]
»	27—495	»	35	(3.19)	M_w; S, LS	[154]
» (M_w/M_n 1.02–1.14)	208—1010	»	35	**3.33±0.08	M_w; S, D, LS	[34]
»	208—1010	»	35	(3.25)	M_w; S, D, LS	[154]
» "S105" (M_w/M_n 1.05)	160	»	35	3.08	M_w; S, LS	[161]
» "Waters prod. No. 25170" (M_w/M_n 1.04)	51	»	15—35	3.03±0.04	M_w; S, LS	[162]
»	1500	»	32—42	2.93±0.07	M_{η}; S	[162]
» (M_w/M_n 1.03–1.12)	109—422	»	35	3.07±0.09	M_w; S, LS, OS	[156]
» "narrow fractions"	10—2200	»	34.5	3.28±0.03	M_w; S, LS	[163]
» (M_z/M_w 1.19)	118	»	35	**3.82	M_w; S, LS, SF	[63]

*, **As for Table 5.

Table 6 contains results for fractions of flexible-chain polymers analogous to those in Table 5 but obtained for solutions in θ-solvents. The average value over all 26 systems (total number of fractions 137) is $A_0 = (3.2 \pm 0.2) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$, the same as that obtained in "good" solvents (Table 5).

Values obtained both in thermodynamically "good" solvents and in θ-solvents are given in Tables 5 and 6 for several of the polymers (denoted by a pair of asterisks **). Comparison shows that for the same fractions the experimental value of A_0 under θ-conditions may be either slightly greater or slightly smaller than A_0 in a "good" solvent. However, these differences are no greater than those in A_0 in different θ-solvents or in different "good" solvents, and lie within the limits of experimental error.

Thus it can be concluded from Tables 5 and 6 that excluded-volume effects have no appreciable influence on the value of A_0.

Experimental information on the influence of molecular-mass polydispersity on A_0 is rather meagre. Several results are given in Table 7, which compares values of A_0 for the initial unfractionated specimens and those obtained from their fractions. The number of polymers is 14, and the total number of fractions 203. Table 7 reveals no unambiguous independence of A_0 on polydispersity, since in about half the cases A_0 is greater for the unfractionated specimen than for the corresponding fractions, whereas for the other half the opposite relation is found. The observed differences lie within the limits of experimental error, and therefore may in general be disregarded. These results are consistent with the theoretical conclusions[29] mentioned above: for moderately polydisperse polymers ($M_w/M_n < 2$) only a slight dependence of A_0 on the width of the molecular-mass distribution can be expected.

Table 8 lists experimental values of A_0 obtained for fractions of polymers whose molecules have a ladder or semi-ladder structure. They cover 31 different polymer–solvent systems with a total of 351 fractions. The mean is

Table 7. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for fractions and unfractionated initial specimens (u.i.s.).

Polymer (degree of substitution)	Fractions and specimens	M	$10^{10}A_0$	Ref.
Poly(vinyl cinnamate)	13 fractions	M_{SD} = 51 000 – 762 000	3.58±0.10	[60]
ditto	u.i.s.	M_{SD} = 223 000	3.51	[60]
Poly-2,5-(4′,4″-diphenylene phthalide)-1,3,4-oxadiazole	10 fractions (M_w/M_n 1.14–1.31)	M_w = 8500—855 000	3.12±0.35	[164]
ditto	u.i.s. (M_w/M_n 3)	M_w = 227 000	2.60	[164]
Polyisobutylene	9 fractions ($M_w/M_n \geqslant 2$)	M_w = 9700—308 000	3.46±0.25	[64]
ditto	u.i.s.	M_w = 77 500	2.83	[64]
Poly-*m*-phenyleneisophthalamide	8 fractions	M_{SD} = 8000 – 250 000	3.74±0.26	[165]
ditto	u.i.s.	M_{SD} = 142 000	3.65	[165]
»	48 fractions (M_z/M_w 1.2–1.4)	M_{SD} = 1300—305 000	3.59±0.05	[166]
»	u.i.s. (M_w/M_n 1.8)	M_{SD} = 113 000	3.73	[166]
Cellulose nitrate (1.9)	7 fractions	M_{SD} = 15 900—78 300	3.23±0.07	[167]
ditto (1.9)	u.i.s.	M_{SD} = 65 000	3.54	[167]
» (2.7)	13 fractions	M_{SD} = 56 000—983 000	3.23±0.05	[168, 169]
» (2.7)	u.i.s. (M_z/M_w 1.36)	M_{SD} = 335 000	3.36	[168, 169]
» (2.31)	27 fractions	M_{SD} = 60 000 – 813 000	3.40±0.05	[170]
» (2.31)	u.i.s. (M_z/M_w 1.4)	M_{SD} = 470 000	3.47	[170]
» (2.4)	10 fractions (M_z/M_w 1.19 ± 0.07)	M_{SD} = 25 600—282 000	3.61±0.19	[171]
» (2.4)	u.i.s. (M_z/M_w 1.45)	M_{SD} = 169 000	3.56	[171]
» (1.2)	8 fractions	M_{SD} = 67 000—566 000	3.15±0.19	[171]
» (1.2)	u.i.s.	M_{SD} = 261 000	3.20	[171]
» (2.0)	12 fractions	M_{SD} = 5500—51 400	3.39±0.13	[172]
» (2.0)	u.i.s.	M_{SD} = 23 200	3.57	[172]
Poly-(2-triphenylmethoxyethyl methacrylate)	15 fractions (M_z/M_w 1.16 ± 0.07)	M_{SD} = 68 000—5 200 000	2.85±0.13	[127]
ditto	u.i.s. (M_w/M_n 2.9, M_z/M_w 2.3)	M_{SD} = 100 000	3.00	[127]
Polychlorophenylsiloxane, ladder	20 fractions	M_{SD} = 33 500—4 230 000	3.05±0.17	[173]
ditto	u.i.s.	M_{SD} = 454 000	2.90	[173]
Poly(ethylene terephthalate)	6 fractions (M_{SD}/M_n 1.08 ± 0.09)	M_{SD} = 25 000—111 000	3.58±0.24	[100]
ditto	u.i.s.	M_{SD} = 87 300	2.51	[100]

$A_0 = (3.14 \pm 0.13) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$, which coincides within the limits of experimental error with the corresponding experimental value for flexible-chain polymers (Tables 5–7), although ladder polymers are characterised by increased equilibrium rigidity of the molecular chains, which may exceed several times the rigidity of flexible-chain polymers[17]. This difference in rigidity is apparently insufficient, while the molecular masses of polymers in Table 8 are too large, for experiments to be able (in conformity with the predictions of theory, Figs.1 and 2) to detect a difference in the values of A_0 for more rigid polymers (Table 8) and for more flexible polymers (Tables 5–7).

Table 9 contains experimental values of A_0 for derivatives of cellulose and other polysaccharides, obtained for 62 polymer–solvent systems with a total of 428 fractions. They can conveniently be divided into two groups, applying respectively to solutions in organic solvents and to aqueous and buffer systems. If values in organic solvents are averaged, obtained by light-scattering and sedimentation methods, the result is $A_0 = (3.30 \pm 0.23) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$, whereas averaging in the first group of values, obtained by sedimentation and diffusion methods, yields $A_0 = (3.32 \pm 0.32) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. These two values are almost identical, and agree within the limits of

Table 8. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for polymers having a ladder or semi-ladder molecular structure.

Polymer	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0$	Type of M; methods	Ref.
		Ladder polymers				
Polydichlorophenylsiloxane	42—540	benzene	24	3.21±0.17	M_{sD}; S, D	[174]
» (M_z/M_w 1.2–1.6)	42—2200	»	21	3.05±0.20	M_{sD}; S, D	[175]
Poly-3-methylbut-1-enylsiloxane	92—600	butyl acetate	24	3.11±0.10	M_{sD}; S, D	[176]
»	3.5—740	»	24	3.04±0.18	M_{sD}; S, D	[177]
Polyphenylisobutylsiloxane 1:1	13—2290	»	24	3.42±0.15	M_{sD}; S, D	[178]
»	13—2290	»	24	3.48	M_{sD}; S, D	[179]
Polyphenylisohexylsiloxane 1:1	6.1—386	»	24	3.26±0.21	M_{sD}; S, D	[178]
Polyphenylsiloxane, TsLFS-3	40—3350	benzene	21	3.30±0.25	M_{sD}; S, D	[179]
ditto	40—3350	»	21	2.71	M_{sD}; S, D	[17]
», TsLFS-1	37—420	»	21	3.22±0.12	M_{sD}; S, D	[180—182]
», TsLFS-2	17—311	»	21	2.73±0.15	M_{sD}; S, D	[180—182]
», (M_z/M_w 1.38 ± 0.16)	25—750	»	22	3.23±0.20	M_w; S, D, LS	[183]
», specimen A	15—430	»	24	3.08±0.16	M_{sD}; S, D	[184]
», specimen B	9—470	»	24	3.25±0.22	M_{sD}; S, D	[184]
»	34.8—181.5	»	20	(1.70±0.16)	M_w; S, LS	[185]
»	47—753	»	24	3.24±0.14	M_{sD}; S, D	[186]
Polychlorophenylsiloxane	49—1590	»	24	3.24±0.10	M_{sD}; S, D	[187]
»	33.5—4230	»	24	3.05±0.17	M_{sD}; S, D	[173]
		Semi-ladder polymers				
Polyarylate*	12.2—26.8	oxolan	20	3.15±0.19	M_w; S, LS	[188]
Polyarylate**	26.3—107.2	tetrachloroethane	20	3.33±0.16	M_w; S, LS	[188]
Polyacenaphthylene, "PAtsN-1"	10—930	benzene	24	3.10±0.16	M_{sD}; S, D	[189]
"PAtsN-2"	14—1140	»	24	3.10±0.13	M_{sD}; S, D	[189]
», "solid phase"	6—230	»	24	3.20±0.10	M_{sD}; S, D	[190]
Poly-*N*-2,4-dimethylphenylmaleimide	38—198	butyl acetate	21	2.90±0.09	M_{sD}; S, D	[191]
Poly-2,5-(4′,4″-diphenylene phthalide)-1,3,4-oxadiazole (M_w/M_n 1.14–1.31)	8.5—855	dimethylacetamide	20	***3.12±0.35	M_w; S, LS	[161]
Poly-*N*-isobutylmaleimide (M_z/M_w 1.08–1.27)	190—3400	butyl acetate	21	2.90±0.09	M_{sD}; S, D	[192]
Polycarbonate****	1.5—87.8	benzene	21	2.93±0.12	M_{sD}; S, D	[193]
Polycarbonate	8.5—266	oxolan	20	3.52±0.26	M_{sD}; S, D	[194]
Polycarbonate from Bisphenol A (M_w/M_n 1.13 ± 0.05)	4.3—466	»	25	3.33±0.08	M_w; S, LS, OS	[195]
Poly-*p*-tolylmaleimide	40—560	dimethylformamide	21	2.98±0.25	M_{sD}; S, D	[196]
Polyphenylisobutylsiloxane, helical ladder	2.8—750	cyclohexane	24	3.12±0.21	M_{sD}; S, D	[197]
Polyphenylene, methylated	5.5—270	toluene	20	2.98±0.14	M_{sD}; S, D, OS	[198]

*Polyarylate based on sebacoyl chloride and 3,3-bis-*p*-hydroxyphenylphthalide.

**Polyarylate based on terephthaloyl chloride and 9,9-bis-*p*-hydroxyphenylfluorene.

***Sedimentation constants s_0 from concentration dependence[164] of s on c recalculated with mean $k_s/[\eta] = 1.7$ by means of the equation $s_0 = s(1 + kc)$.

****Polycarbonate based on 1,1-di-*p*-hydroxyphenylcyclohexane.

Table 9. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for cellulose, amylose, their ethers, esters, and copolymers, and other polysaccharides.

Polymer (degree of substitution)	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0$*	Type of M; methods	Ref.
		Solutions in organic solvents				
Amylose, unsubstituted, M_z/M_w 1.28	34—2630	dimethyl sulphoxide	25	2.87±0.36	M_w; S, LS	[199]
Cellulose acetate, "narrow" fractions	10.4—194	acetone	20	3.25±0.15	M_{sD}; S, D	[200]
ditto	10.4—194	»	20	(3.60)	M_n, $\upsilon = 0.74$	[6]
», 53.8% acetate groups, M_sD/M_n 1.11 ± 0.14	23—123	»	20	3.70±0.23	M_{sD}; S, D, OS	[201]
», (2.34)	26—150	»	25	(5.7±0.6)	M_n; S, OS	[202]
Cellulose benzoate (2.3 ± 0.1)	51—660	dioxan	26.6	2.7±0.5	M_{sD}; S, D	[203]
Cellulose diphenylphosphonocarbamate (2.3 ± 0.5)	1—1670	»	26.6	3.1±0.5	M_{sD}; S, D	[203]

Table 9 (cont'd.).

Polymer (degree of substitution)	$10^{-3} \cdot M$	Solvent	Temp., °C	$10^{10} A_0^*$	Type of M; methods	Ref.
Cellulose monophenylacetate (2.6 ± 0.2)	65—5410	benzene	26	3.15±0.30	M_{sD}; S, D	[203]
Cellulose nitrate, 10.5-12.25% N	6.2—613	acetone	20	2.67±0.36	M_{sD}; S, D	[204]
ditto 11.10-13.98% N	13.8—1175	»	20	3.47±0.28	M_{sD}; S, D, SE, OS	[205]
», 13.1-13.8% N	74.5—2490	»	21	3.71±0.22	M_{sD}; S, D	[206]
», (2.88)	13—2490	»	20	4.14±0.31	M_{sD}; S, D	[207]
»	190—344	»	20	3.67±0.15	M_{sD}; S, D	[208]
»	76—1400	»	20	3.75±0.34	M_w; S, LS	[209]
», (1.9)	15.9—78.3	butan-2-one	25	3.23±0.07	M_{sD}; S, D	[167]
», (3), M_{sD}/M_n 1.36 ± 0.11	93—1500	ethyl acetate	20	4.30±0.66	M_{sD}; S, D, OS	[210]
», (2.84), M_z/M_w 1.35 ± 0.14	41.3—573	»	30	3.32±0.19	M_w; S, LS, OS	[211]
», (2.7)	56—983	»	21	3.23±0.05	M_{sD}; S, D	[168, 169]
», (2.31 ± 0.05), M_w/M_n <1.5	60—813	»	25	3.40±0.05	M_{sD}; S, D	[170]
», (2.39 ± 0.03), M_z/M_w 1.19 ± 0.07	25—282	»	25	3.61±0.19	M_{sD}; S, D	[171]
», RS1/8, 11% N	5.5—51.4	»	25	3.39±0.13	M_{sD}; S, D	[172]
», (1.15 ± 0.10)	67—566	DMA-6% LiCl	25	3.15±0.19	M_{sD}; S, D	[171]
Polysaccharides, synthetic, stereoregular						
tribenzyl(1-6)-α-glucan	180, 867	benzene	8	2.66±0.40	M_w; S, LS	[212]
tribenzyl(1-6)-α-mannan	524, 685	»	8	3.52±0.32	M_w; S, LS	[212]
tribenzyl(1-6)-α-galactan, M_w/M_n 2-3	189—922	»	8	3.38±0.40	M_w; S, LS	[212]
Cellulose tributyrate (2.94), M_w/M_{sD} 1.2	74—1700	bromoform	20	3.37±0.20	M_{sD}; S, D	[213]
ditto	74—1700	»	20	(3.40±0.13)	M_w; D, LS	[214]
»	63—1700	butan-2-one	20	3.32±0.13	M_{sD}; S, D	[213]
»	63—170	»	20	(3.40±0.20)	M_w; D, LS	[214]
Cellulose tributyrate-2-methyl-5-vinylpyridine 15-71%, M_z/M_w 1.2-1.4	130—940	»	20	2.36±0.84	M_{sD}; S, D	[215, 216]
Cellulose phenylcarbamate	105—1399	acetone	20	3.59±0.50	M_w; S, LS	[209]
ditto (3), M_w/M_n 1.10 ± 0.05	1.28—2580	1.4-dioxan	20	3.42±0.07	M_{sD}; S, D	[217]
», (2.1 ± 0.1)	14—107	»	23	3.62±0.24	M_{sD}; S, D	[218—220]
», (3), M_w/M_n 2.01	170—1085	cyclohexanone	25	2.31±0.08	M_w; S, LS, OS	[221]
»	170—1085	»	25	(1.48)	M_w; S, LS, OS	[221]
», (2.2)	20—920	ethyl acetate	23	3.35±0.23	M_{sD}; S, D	[222]
», (2.5)	2600	»	2.5—50	2.73±0.30	M_{sD}; S, D	[223]
», (2.67)	152—2600	»	25	3.09±0.21	M_{sD}; S, D	[224]
Ethylcelluose (2.75)	11.45—78.3	acetone	20	3.42±0.05	M_{sD}; S, D	[225]
», unfractionated, M_z/M_w = 1.10-1.19	27.5—67.5	ethyl acetate	20	3.54±0.32	M_{sD}; S, D	[226]
», (2.27)	5—31	»	24	3.73±0.12	M_{sD}; S, D	[227]
		Aqueous and buffer systems				
Amylose from potatoes	160—2290	0.33 M KCl	20	2.79±0.05	M_w; S, LS	[228]
Amylose tricarbanilate, M_w/M_n 1.5	300—2440	pyridine-water 86.71:13.29	25	2.98±0.14	M_w; S, LS	[229]
Hydroxypropylcellulose M_{sD}/M_n 2.1	73	water	25	3.77	M_{sD}; S, D, OS	[230]
»	73	»	25—40	3.87±0.07	M_{sD}; S, D, OS	[231]
Hydroxyethylcellulose	160—570	»	25	4.2±0.3		[232]
ditto (0.88), M_w/M_n 1.65 ± 0.07	190—625	»	25	4.04±0.16	M_n; S, D, LS, OS	[233]
»	190—625	»	25	(4.48±0.07)	M_{sD}; S, D, LS, OS	[233]
»	190—625	»	25	(4.78±0.12)	M_w; S, D, LS, OS	[233]
», Natrasol 250 G	150	»	25	4.06	M_{sD}; S, D	[230]
Dextran	14—38000	0.025 M Na_2HPO_4 + 0.025 M NaH_2PO_4	20	2.86±0.14	M_{sD}; S, D	[234]
», NRRL B-512, hydrolysed, M_w/M_n 1.25 ± 0.11	17.7—2700	water	20	2.73±0.18	M_w; S, LS	[235]
», B-512-Ph and A-179, 5-30% branched units, M_w/M_n 1.4-1.6	11.2—437	0.05 *N* Na_2HPO_4+0.05 *N* NaH_2PO_4	20	3.17±0.14	M_{sD}; S, D, LS (M_n)	[236]
Cellulose dimethylphosphonocarbamate (urethanecellulose) (2.0)	200—2400	0.2 *M* NaCl	22	4.36±0.41	M_{sD}; S, D	[237]
Carboxymethylcellulose (0.69 ± 0.04)	44.7—346	0.1 *M* NaCl	25	4.90±0.25	M_{sD}; S, D	[238]
Lignin, alkali	290—1860	$NaHCO_3$-NaOH buffer	25	3.18±0.54	M_w; S, LS	[239]
Methylcellulose	22.6—302	water	20	3.21±0.16	M_{sD}; S, D	[240]
Levan polysaccharide from *S. salivarius*, $M_w/M_n \leqslant 1.08$	17400—29700	»	25	2.89±0.20	M_w; S, LS	[241]
», partly hydrolysed	9.96—42800	»	25	2.92±0.87	M_w; S, LS	[242]
Schizophyllan, native polysaccharide, M_z/M_w 1.4 ± 0.1	96—5700	»	25	4.24±0.21	M_w; S, LS	[243]
Ficoll-400 synthetic polysaccharide	400	»	25	(1.00)	M_w; S	[230, 244]
Proteoglycan, bovine nasal cartilage	1000—2400	4M guanidine HCl	20	3.24±0.57	M_w; S, LS	[245]
Galactomannan polysaccharide	152—657	0.025 M KH_2PO_4 + 0.025 M Na_2HPO_4	20	(4.8±0.1)	M_{sD}; S, D_A	[246]
Sulphoethylcellulose, Na salt	80—310	0.1 M NaCl	21	3.60±0.29	M_{sD}; S, D	[247]
Chitosan	14.2—160	trifluoroacetic acid	25	3.04±0.31	M_w; S, SE	[248]
Cellulose, M_w/M_n ~2	42.2—747	Cadoxene-water 1:1	25	3.80±0.08	M_{sD}; S, D	[249]
» M_w/M_n 1.9 ± 0.2	10.1—33.7	»	25	2.95±0.13	M_w; S, LS, SE, OS	[250]
», linters, M_z/M_w 1.6 ± 0.5	2—700	»	20	3.73±0.33	M_{sD}; S, D	[251]
»	500 and 560	»	20	3.84	M_{sD}; S, D	[252]
Cellulose-acrylamide 78-94%, M_z/M_w 1.2 ± 0.2	240—4030	»	20	3.55±0.35	M_{sD}; S, D	[252, 216]
Ethylhydroxyethylcellulose (0.56 C_2H_5O, 0.84 C_2H_4O), M_w/M_n 3, M_{sD}/M_n 1.7	92—310	water	20	4.23±0.17	M_{sD}; S, D, LS, OS	[253]

*Values of A_0 in parentheses disregarded in calculation of mean values of A_0.

Table 10. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for rigid-chain polymers.

Polymer	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0$*	Type of M; methods	Ref.
Rigid-chain polyamides and heterocyclic polymers						
Polyamide-benzimidazole	9.5—60.9	dimethylacetamide	25	3.55±0.15	M_{sD}; S, D	[255]
»	6.6—72	»	25	3.81±0.45	M_w; S, SE	[256]
Polyamide-benzoximidazole	10—24.3	dimethylacetamide-3% LiCl	25	3.55±0.20	M_{sD}; S, D	[76]
Polyamide-hydrazide	5—34	dimethylacetamide	24	3.67±0.33	M_{sD}; S, D	[257]
ditto	3.63—47.7	»	24	(4.19±0.44)	M_w; D, LS	[257, 258]
»	21—34	dimethyl sulphoxide	24	3.80±0.05	M_{sD}; S, D	[257]
»	3.63—47.7	»	24	(4.07±0.27)	M_w; D, LS	[257, 258]
Poly-*p*-benzamide	7—18	96% H_2SO_4	25	3.60±0.07	M_w; D, LS	[259]
ditto, non-mol. soln.	9—80	dimethylacetamide-3% LiCl	25	(4.5±0.5)	M_{sD}; S, D	[259]
»	13.8—52.5	»	25	(3.2±0.1)	M_w; S, SE	[260]
Poly(butyl isocyanate)	3.8—1380	tetrachloromethane	24	4.16±0.45	M_{sD}; S, D	[261]
»	18—211	oxolan	20	(2.00±0.16)	M_{sD}; S, D	[262]
Poly(hexyl isocyanate) $M_z/M_w \leqslant 1.05$	68—7240	hexane	25	3.60±0.10	M_w; S, LS	[263]
Poly(chlorohexyl isocyanate)	12—306	tetrachloromethane	20	3.84±0.16	M_{sD}; S, D	[264]
Polybistri-*t*-butylphosphineplatinum-buta-1,4-dienediyl, $M_w/M_n \sim 1.1$	20.6—141	heptane	25	3.66±0.12	M_w; S, LS	[265]
Tobacco mosaic virus	33 200	0.01 M NaCl	20	3.63	M_{sD}; S, D	[266, 267]
Poly-(γ-benzyl *L*-glutamate)	37—332	dimethylformamide	20	4.15±0.16	M_w; S, D, LS	[268, 269]
ditto	37—332	»	20	4.00±0.13	M_{sD}; S, D	[268, 269]
»	42—364	»	21	3.99±0.55	M_{sD}; S, D	[270, 271]
», M_w/M_n 2.12 ± 0.26	17.6—394	»	25	3.34±0.12	M_w; S, SE, OS	[272, 273]
»	18.5—414	»	25	(3.18±0.12)	M_w; S, LS	[272]
»	34.7—414	»	25	3.27±0.20	M_w; S, SE	[274, 273]
»	36.4—435	»	25	(3.11±0.20)	M_w; S, LS	[274]
»	200—500	»	25	5.20±0.62	M_w; D, LS	[275]
», P. Ch. № G-100	320	»	25	3.98	M_w; S	[276]
»	37—659	»	25	3.68±0.13	M_{sD}; S, D	[76]
Poly-(ε-benzoxycarbonyl-*L*-lysyl-γ-benzyl *L*-glutamate), M_w/M_n 1.18-1.34	77.9—476	dimethylformamide	25	3.69±0.10	M_w; S, LS	[273]
Poly-$N_{(5)}$-3-*hydroxypropyl-L-glutamine, partial* helix	19—140	water	20	3.86±0.14	M_{sD}; S, D	[277]
ditto	53.5—333	»	25	3.13±0.09	M_w; S, LS, SE	[278]
», helix	19—140	methanol	20	4.03±0.26	M_{sD}; S, D	[277]
»	26.9—333	»	25	3.51±0.27	M_w; S, LS, SE	[278]
DNA, native, calf thymus	7700	0.15 M NaCl+0.015 M $C_6H_5O_7Na_3$ (citrate buffer)	20	4.14	M_w; S, LS	[279, 280]
ditto, ultrasonically degraded fragments	300—7400	0.2M NaCl, citrate buffer or 0.0025M Na_2HPO_4 + 0.005M NaH_2PO_4 + 0.001M $EDTANa_2$	20	3.74±0.09	M_w; S, LS	[281, 282]
»	300—7400		20	(4.3±0.5)	M_w; S, LS	[281]
»	300—7400	»	20	(3.78±0.30)	M_w; S, LS	[281, 283]
», mechanically degraded fragments M_w/M_n 1.44-2.32	1950—14100	0.006M Na_2HPO_4 + 0.002M NaH_2PO_4 + 0.001M $EDTANa_2$ + 0.0179M NaCl	20	3.68±0.07	M_{sD}; S, D	[282]
ditto	8900	buffer solution	20	3.70	M_{sD}; S, D	[284]
», *D. pneumoniae*	1250—2860	»	20	3.71±0.09	M_w; S, LS	[285]
»	1800 and 5000	»	20	4.12±0.16	M_w; S, LS	[283]
»	16 000	»	20	3.3	—	[286]
», Herring sperm	570—6200	»	20	3.68±0.12	$(M_{sD})_w$; S, D	[287, 288, 283]
», P. mirabilis	30 600	»	20	3.51	—	[289]
», Salmon sperm	6300	»	20	4.76	M_w; S, LS	[290]
», bacteriophage T7	24 600	»	20	3.55	M_w; S, LS	[291, 292, 282]
»	24 600	»	20	3.35	M_w; S, LS	[292—295, 282]
	25 200	»	20	3.53	M_{sD}; S, D	[296, 284]
»	25 200	(4.2-∞)pM CH_3HgOH + 0.005M Na borate + (0.005-0.5)M Na_2SO_4	20	2.88±0.17	—	[297]
», bacteriophage T4	112 400	0.2 M NaCl	20	3.42	M_{sD}; S, D	[284]
», bacteriophage T3	24 600	buffer solution	20	3.4	M_w; S, LS	[298]
Collagen, native, M_w/M_n 1.11	345	2 M KCNS	20	4.30	M_w; S, LS, OS	[299]
»	137—374	citrate buffer	24.8	4.49±0.14	—	[300]
»	301 1690	0.06 M K acetate buffer	—	4.32±0.39	M_w; S, SE	[301]
Poly-(*L*-lysine HBr)	128	1.0 M NaCl	25	3.59	M_w; S, SE	[302]
», $[Lysine]_n$>0.4 g dl^{-1}	240	0.5 M Na_2CO_3 + 0.5 M $NaHCO_3$	25	3.33	M_w; S, SE	[302]
», $[Lysine]_n$<0.4 g dl^{-1}	126	»	25	3.90	M_w; S, SE	[302]
Polymers with semi-rigid aromatic chains						
Polyamide-ester, aromatic	7.8—125	dimethylformamide	25	3.89±0.52	M_w; S, LS	[303]
Poly-4,4'-diphenylphthaleinterephthalamide	29.4—1110	»	25	3.67±0.14	M_w; S, SE	[304]
Poly-4',4''-diphenylenephthalidepyromellitimide	8.2—51.6	»	25	4.56±0.23	M_w; S, LS	[303]
Polyimide**	20—280	dimethylacetamide	25	3.73±0.40	M_{sD}; S, D	[305]
Polyimide***	20—1400	»	20	2.94±0.27	M_w; S, SE	[306]
Poly-*m*-phenyleneisophthalamide, M_z/M_w 1.2-1.4	4.3—165	»	26	3.40±0.33	M_{sD}; S, D	[76]
ditto	74	DMA-0.25% LiCl	25	3,1	M_w; S, LS	[307]
»	8—250	DMA-3% LiCl	25	3.74±0.26	M_{sD}; S, D	[308]
»,	4,3—306	»	25	3.59±0.05	M_{sD}; S, D	[309]
Polysulphonamide****	25—106	dimethylacetamide	25	3.36±0.08	M_w; S, SE	[310]
Poly(tolyl isocyanate)	32—152	acetone	24	3.93±0.09	M_{sD}; S, D	[311]
Polyphenylquinoxaline	24—370	*N*-methylpyrrolidone	25	3.85±0.06	M_w; S, SE	[312]
»	6—120	tetrachloroethane	21	3.06±0.20	M_{sD}; S, D	[313]
Polyphthaloyl-*trans*-2,5-dimethylpiperazine	13.1—406	*N*-methylpyrrolid-2-one	25	3.94±0.33	M_w; S, LS	[314]
»	13.1—160	dimethylacetamide	25	3.47±0.18	M_w; S, LS	[314]

*Values of A_0 in parentheses disregarded in calculation of mean experimental values of A_0.

**Polyimide based on diaminodiphenylmethylphenylmethane and oxydiphenyl-3,3',4,4'-tetracarboxylic acid.

error with the value for flexible-chain polymers. This is not unexpected, since the rigidity of the molecular chains of cellulose derivatives, though greater than for flexible-chain polymers, is close to that of the ladder polymers considered above.

A rather different situation is found for the second group of values, obtained in aqueous and buffer solutions of polysaccharides. The mean obtained by light-scattering and sedimentation is $A_0 = (4.02 \pm 0.38) \times 10^{-10}$, but the use of sedimentation and diffusion gives a mean of $A_0 = (3.50 \pm 0.80) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. Both values exceed that obtained in organic solvents, and are characterised by a greater experimental error. This illustrates the difficulties of working with aqueous and buffer solutions, especially when the sedimentation–diffusion method is used together with Eqn.(15).

In Table 10 data have been assembled on rigid-chain polymers, which are divided into three classes. The first comprises rigid-chain aromatic polyamides, polyamides having heterocycles in the chain, and poly(alkyl isocyanates), whose molecules have high equilibrium rigidity characterised by a Kuhn segment length 500–600 Å.[228] Polymer molecules in the second class are no less rigid than those in the first class, but the rigidity is due to the presence of a secondary structure leading to a helical chain conformation[1]. Finally, the third class comprises compounds, mainly also aromatic, arbitrarily termed "semi-rigid". Although the Kuhn segment length for their chains is smaller than for molecules of the first two classes[228], it is sufficient to ensure considerable permeability of the molecular coil in solution, which should increase the parameter A_0. This is confirmed on comparing values in Table 10 for the three classes of polymers.

The total number of polymer–solvent systems covered in Table 10 is 61, and the total number of fractions investigated 412. The mean over all polymers and fractions is $A_0 = (3.7 \pm 0.4) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. The averaging excluded values for specimens No.7 and 8, solutions of which are not molecularly disperse. As with cellulose derivatives, the error in determination of A_0 is appreciably greater for rigid-chain than for flexible-chain polymers, as a consequence of specific experimental difficulties in working with solutions of the polymers in Table 10. Yet the average value of A_0 exceeds considerably that for flexible-chain polymers, and this difference is real, since it lies outside the experimental error. For all specimens in Table 10 (other than No.9) the parameter A_0 was invariant in the series of fractions investigated. For fractions of poly(butyl isocyanate) (No.9), investigated over a wide range of molecular weights, A_0 increased with decrease in chain length L. This can be regarded as confirmation of the theoretical predictions (Fig.1) for a polymer in which d/A is lower than for other polymers.

V. CONCLUSION

The experimental results surveyed in the previous Sections can be summarised in the statement that, for every polymer–solvent system throughout the range of molecular masses accessible to experiment, the parameter A_0 determined from formulae (4), (5), and (15) is indeed invariant, independent of chain length, solvent, and, for moderately polydisperse specimens, their degree of polydispersity.

For all flexible-chain polymers and synthetic polymers having moderately enhanced chain rigidity the most reliable experimental value is

$$(A_0)_{flex} = (3.2 \pm 0.2) \cdot 10^{-10} \text{ erg deg}^{-1} \text{ mole}^{-1/3} = (3.2 \pm 0.2) \cdot 10^{-17} \text{ J deg}^{-1} \text{ kmole}^{-1/3} \quad (16)$$

from which we obtain

$$\beta \equiv P^{-1}(\Phi/100)^{1/3} = 2.3 \cdot 10^6 .$$

These experimental values are considerably lower than those predicted by analytical theories—$A_\infty = 3.8 \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$ and $\beta = 2.71 \times 10^6$—and agree well with those obtained by Zimm's computer experiment[26]—$A_\infty = 3.13 \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$ and $\beta = 2.33 \times 10^6$ (Table 2).

For polymers of high chain rigidity the mean experimental value

$$(A_0)_{rig} = (3.7 \pm 0.4) \cdot 10^{-10} \text{ erg deg}^{-1} \text{ mole}^{-1/3} \quad (17)$$

is identical with that of A_∞ predicted by the analytical theories. However, this experimental value cannot be regarded as A_∞, since it has been obtained for short polymer chains, in several cases with $L/A < 10$. It is more logical to adopt as experimental value of A_∞ the quantity $(A_0)_{flex}$ determined by means of Eqn.(16), since it has been obtained with the maximum chain lengths accessible to experiment. In conformity with this the difference between $(A_0)_{rig}$ and $(A_0)_{flex}$—respectively from Eqns.(17) and (16)—must be regarded as a result of increase in the ratio A_0/A_∞ for a rigid-chain polymer ($d/A \ll 1$) in the region of low values of L/A in conformity with the theory of vermiform chains (Table 1 and Figs.1 and 2).

Thus in the practical utilisation of the present results to determine the molecular mass of a polymer from experimental values of $[\eta]$ and f by means of formulae (4) and (5) the value of A_0 determined by means of formula (16) can be recommended for flexible-chain and moderately rigid-chain polymers, and that obtained from (17) for polymers of high chain rigidity. For derivatives of cellulose and other polysaccharides of adequate purity and molecular dispersity of non-electrolyte solutions Table 9 indicates use of the value $A_0 = (3.30 \pm 0.30) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$, obtaining which, however, has involved considerable error.

As mentioned at the beginning of this Review, use of the invariant A_0 in determining molecular masses M is especially important for polymers of high chain rigidity, which have low molecular mass and also are soluble only in such specific solvents as concentrated sulphuric acid. The combination of all these properties in effect excludes the possibility of using sedimentation and makes light scattering a relatively ineffective method[2]. The most useful combination under these conditions is that of viscometric and diffusion measurements with the use of formula (4) and the above experimental values of A_0. This method is widely used at the present time.

The fact that the experimental A_∞ corresponds to $\beta = 2.3 \times 10^6$ instead of the 2.7×10^6 predicted by theories of sliding friction and viscosity of macromolecules means that the theoretical values $P_\infty = 5.11$ and $\Phi_\infty = 2.8 \times 10^{23}$ mole^{-1} are incompatible. Thus interpretation of experimental data on diffusion (or sedimentation) and on solution viscosity for the same polymer in terms of a single theory of these

Table 10 (cont'd.).

***Polyimide based on oxydiphenyl-3,3′,4,4′-tetracarboxylic dianhydride and 9,9-di-*p*-aminophenylfluorene.
****Polysulphonamide based on di-*p*-aminophenyl sulphone and terephthalic acid.

processes[12,13] cannot yield identical values of chain rigidity (Kuhn segment length). Theories of transport processes in polymer solutions require elaboration, which in turn should eliminate the above inherent contradiction and provide a theoretical value of A_∞ corresponding to experimental results. By means of Zimm's computer experiment[26] it has proved possible to do this by some decrease in the theoretical value of Φ_∞ and a considerable increase in the theoretical value of P_∞. Whether this is the only possible method should appear from further research.

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Phase Structure of Epoxide-Rubber Systems

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Formation of the phase structure during three-dimensional polycondensation in heterophase epoxide-rubber systems is discussed. Aspects of the phase equilibrium and the interdiffusion of the components in the initial systems and during the chemical reaction are examined. A two-stage mechanism of structure formation is suggested. A relation is demonstrated between the thermodynamic affinity of the components and the final phase structure. Possible methods for obtaining systems having specified parameters are considered. A list of 102 references is included.

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I. INTRODUCTION

Current research on the manufacture and application of polymeric materials is commonly aimed at utilising known polymers by combining or modifying them[1,2]. An urgent task is to improve the physicomechanical properties of vitreous solid polymers (to diminish brittleness, increase resilience, enhance resistance to cracking and creep under the influence of the surrounding medium, and lower thermal shrinkage). A most effective way for solving this problem is to produce heterophase compositions by introducing a modifier as particles of a disperse phase into a vitreous polymer matrix[2-6]. The physicochemical properties of the modified polymers depend significantly[2,4-6] on the proportion by volume and the particle size of the disperse phase and on other parameters of the phase structure. However, research in this field does not yet have a general theoretical basis.

The problem of controlling the properties of heterophase compositions cannot be solved without establishing a quantitative relation between the parameters of the phase structure and the physicochemical properties of the composition, nor without knowledge of the mechanism of formation of the phase structure of modified polymers.

The present Review summaries the results of research on phase-structure formation in epoxide—rubber systems. Problems connected with phase equilibrium and interdiffusion of components during three-dimensional polycondensation of the epoxide oligomer are considered separately.

II. PHASE EQUILIBRIUM IN INITIAL SYSTEMS

When a system includes a region of phase separation the compositions of the phases can be calculated from the equality of the chemical potentials of each component in the coexisting phases, with the condition for phase equilibrium that the Gibbs free energy should be a minimum. For a binary system we have[7]

$$\Delta\mu_1' = \Delta\mu_1'', \quad \Delta\mu_2' = \Delta\mu_2''$$

where the primes are used to denote different phases.

Consideration of the thermodynamics of polymer solutions can conveniently start from the Flory—Huggins lattice theory[8-11], in which statistical concepts were used to produce the first quantitative explanation of the thermodynamic properties of the solutions. According to this theory the change in free energy on mixing is given by the expression

$$\Delta G_{mix} = RT[\varphi_1 \ln\varphi_1 + \varphi_2 m^{-1} \ln\varphi_2 + \chi\varphi_1\varphi_2] \quad (1)$$

in which ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer respectively, $m = v_2/v_1$ is the ratio of the molar volumes of polymer and solvent, and χ is a parameter representing the excess free energy of interaction required to transfer one mole of solvent from the pure solvent to the pure polymer phase. The formulae for the changes in chemical potential of solvent and polymer are respectively

$$\begin{aligned} \Delta\mu_1 &= RT[\ln(1-\varphi_2) + (1-1/m)\varphi_2 + \chi\varphi_2^2], \\ \Delta\mu_2 &= RT[\ln(1-\varphi_1) + (1-m)\varphi_1 + m\chi\varphi_1^2]. \end{aligned} \quad (2)$$

Differentiating $\Delta\mu_1$ with respect to ϕ_2 yields the spinodal equation

$$1-(1-m^{-1}+2\chi\varphi_2)(1-\varphi_2) = 0. \quad (3)$$

At the critical point at which the difference between the coexisting phases disappears $(\partial\mu_1/\partial\phi_2)_{p,T}$ and $(\partial^2\mu_1/\partial\phi_2^2)_{p,T}$ vanish. Hence the critical point is characterised by the relations

$$(\varphi_2)_{cr} = 1/(1+m^{1/2}), \quad (4)$$

$$\chi_{cr} = 1/2 + 1/m^{1/2} + 1/2m. \quad (5)$$

From these it follows that the phase diagrams of the solutions are unsymmetrical, and also that $\chi_{cr} \to \frac{1}{2}$ as $m \to \infty$. Flory termed the critical point at which $m = \infty$ the *θ-point*.

Later research established a quantitative relation between critical temperature and degree of polymerisation[12]. The interaction parameter comprises enthalpy and entropy components[9,12-14]:

$$\chi = \chi_H + \chi_S = -\frac{\Delta H_1}{RT\varphi_2^2} - \frac{\Delta S_1}{R\varphi_2^2}. \quad (6)$$

As $m \to \infty$ we have

$$T_{cr} = \theta \text{ and } \frac{\Delta H_1}{R\theta\varphi_2^2} = \frac{1}{2} + \frac{\Delta S_1}{R\varphi_2^2} \equiv \Psi. \quad (7)$$

Simultaneous solution of Eqns.(4)-(7) yields

$$\frac{1}{T_{cr}} = \frac{1}{\theta}\left[1 + \frac{1}{\Psi}\left(\frac{1}{m^{1/2}} + \frac{1}{2m}\right)\right]. \quad (8)$$

The Flory-Huggins theory proved extremely useful for analysing a large number of experimental results. Despite all its undoubted merits, however, this theory has several defects. The most significant consists in ignoring the concentration dependence of the parameter χ, and also the changes in volume of the components accompanying mixing. The limited character of the lattice theory was noted repeatedly by Flory, who later suggested an improved theory of polymer solutions[15-17].

A vast amount of information has now been accumulated experimentally on the miscibility of components of binary systems. The majority of this research has been done on systems comprising liquids of low molecular weight and also on solutions of polymers. Polymer–oligomer and oligomer–oligomer systems have been studied least[18-29]. Noteworthy among such work has been the use of thermochemical measurements to calculate[18,19] the concentration dependence of the main thermodynamic functions of mixing for a system comprising an epoxide oligomer and a polymeric butadiene-nitrile rubber. The free energy of mixing proved to be negative throughout the composition range, but the concentration dependence was complicated, showing over a certain range a convex curve characteristic of a metastable state. It was concluded that the systems investigated comprised components of limited miscibility.

Phase equilibrium in systems comprising an oligomeric ester-acrylate and an elastomer has been studied[21,22] by an interference method[23]. Examination of the compatibility of polyisoprene with various ether-acrylate oligomers has established the presence of an upper consolute temperature, with the range of compatibility depending on the number of functional groups in the molecule and also on the chemical nature and length of the oligomeric block. Application of the Flory–Huggins theory gave an analytical dependence enabling such lengths to be calculated at which the acrylate end-groups have no effect on the compatibility of the components.

Table 1. Thermodynamic parameters* of ED-20–rubber systems[29].

Rubber	χ^{298}	χ_S	χ_H^{298}	δ_2, cal$^{1/2}$ cm$^{3/2}$	
				expt.	calc.
PB (M_w = 25 000)	2.22	−0.96	3.18	7.5	7.6
OB-KGG(M_n = 2 200) **	1.48	−0.56	2.04	7.9	7.8
OB-KGG(M_n = 3 100)	1.46	−0.50	1.96	8.0	7.7
OB-KGG(M_n = 4 240)	1.49	−0.42	1.91	8.0	7.7
OB-KG (M_n = 3 100)	1.82	−2.35	4.17	7.1	8.1
PDI-1 (M_n = 3 500)	1.86	−0.64	2.50	7.8	7.9
PDI-3A (M_n = 3500)	1.52	−0.52	2.04	8.0	8.3
SKN-8KKG (M_n = 3 100)	0.75	−0.10	0.85	8.6	8.4

* Relative error in determination of the parameters does not exceed 10%.

** M_n = number-average molecular mass.

Hydroxylated oligomeric systems have been studied[24] on mixtures of oligo(propylene glycol) with oligo(ethylene adipate), poly(ethylene glycol), and oligobutadiene, of molecular mass M respectively 1050, 2000, 15 000, and 2360. Reverse gas chromatography was used to measure the retention volume of the sorbate at various temperatures, and then the thermodynamic parameters of mixing were calculated. Results for the compatibility of the components were compared with those predicted by the classic Flory-Huggins theory and the new Flory theory of liquid mixtures. It was found[24] that the thermodynamics of mixing of the oligomers was qualitatively more correctly described by the new theory. However, the concentration dependence of the thermodynamic functions of mixing proved to be extremely complicated, and quantitative agreement between experimental results and theoretical calculations was not observed, which was attributed to the influence of intermolecular interactions (hydrogen bonding) on structure formation.

Oligosiloxanes and oligoisobutenes showed no significant change in component volumes on mixing[26]. The observed heat of mixing was slightly dependent on temperature, which permitted application of the classic Flory-Huggins theory to this system. A non-monotonic dependence of χ on mixture composition was obtained on the assumption that this parameter was enthalpic in nature. The most important result[26] was the need to take into account a non-combinatorial entropy contribution to χ. The oligobutadiene-oligostyrene system showed[27] qualitative confirmation of the main principles of Scott's theory[28], a development of the classic Flory-Huggins theory to apply to polymer mixtures.

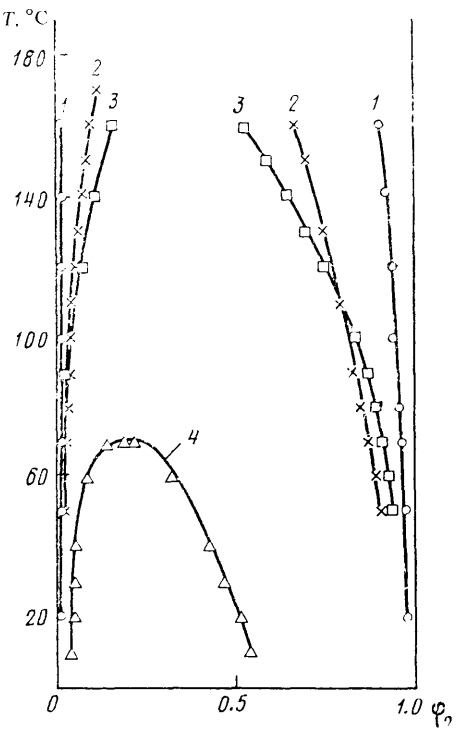


Figure 1. Phase equilibrium diagrams[29] for systems comprising ED-20 with different brands* of rubber: *1*) PB; *2*) OB-KGG with terminal hydroxy-groups; *3*) OB-KKG with terminal carboxy-groups; *4*) SKN-8KKG.

The first investigation of phase equilibrium in systems comprising an epoxide oligomer and an oligomeric rubber established[29] that the introduction of polar groups improves the compatibility of an oligobutadiene (OB) with an epoxide component (Fig. 1). Use of the binodal equation[2]

$$\chi = \frac{\ln(\varphi_1'/\varphi_1'') + (1 - v_1/v_2)(\varphi_2' - \varphi_2'')}{m_1[(\varphi_2'')^2 - (\varphi_2')^2]} \qquad (9)$$

(in which ϕ_1 and ϕ_2 are the respective fractions by volume of ED-20 and an oligomeric rubber, v_1 and v_2 are their molar volumes, $m_1 = v_1/v_0$ with v_0 the molar volume of a segment, and the single and double primes denote symbols corresponding to the two phases in equilibrium) to calculate thermodynamic interaction parameters χ (Table 1) showed a linear dependence on the reciprocal of the absolute temperature. From this relationship χ_H and χ_S were calculated. The equation[30,31]

$$\chi_H = \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \qquad (10)$$

where $\delta_1 = 9.9$ cal$^{1/2}$ cm$^{-3/2}$ is the solubility parameter of ED-20, has been used to calculate values of the corresponding parameter δ_2 for the rubber. Table 1 shows satisfactory agreement with values determined from the theory of group contributions[32]. The carboxylated oligobutadiene (OB-KG) is an exception, apparently owing to marked initial association of the rubber molecules. Such an explanation is supported by the large negative absolute value of χ_S and also by inversion of the binodals of the hydroxylated and carboxylated oligobutadienes at ~100 °C (Fig. 1).

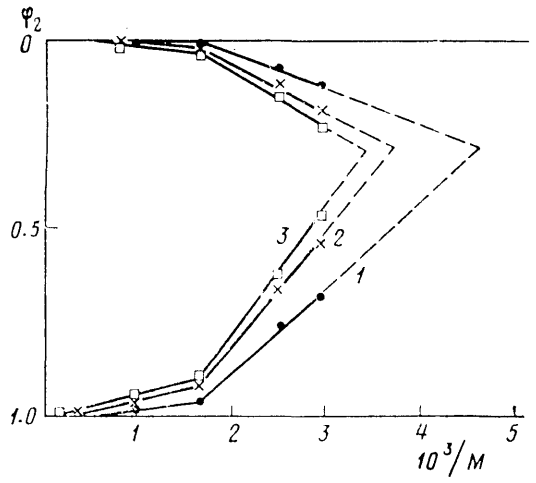


Figure 2. Dependence[6] of solubility of components on molecular mass of epoxide oligomer in ED-20–OB-KGG ($M_n = 2200$) at different temperatures (°C): *1*) 120; *2*) 160; *3*) 180.

Miscibility diminishes with increase in molecular mass of a component, while the upper consolute temperature rises. The influence of molecular mass on phase equilibrium is especially clearly evident in graphs of the dependence of solubility on molecular mass at constant temperature (Fig. 2). On such a diagram two-phase regions are located within the solubility curves, and solutions outside them. With rise in temperature (Fig. 2) and increase in polarity of the oligomeric rubber the region of phase separation becomes smaller. A noteworthy feature of Fig. 2 is the presence of breaks on the graphs. The apparent explanation is that the role of specific intermolecular interactions becomes more important with increase in molecular mass of the epoxide oligomer (EO), which is accompanied by increase in the number of hydroxy-groups in its molecule. The simultaneous improvement in miscibility due to formation of hydrogen complexes partly balances its diminution due to increase in molecular mass of the epoxide. Thus in the presence of specific interactions between the components constancy of δ_{EO} is not a sufficient condition to determine the dependence of the miscibility limits of the components on its molecular mass. The influence of these interactions on the thermodynamics of mixing becomes weaker on passing to lower epoxide oligomers.

III. INTERDIFFUSION IN INITIAL SYSTEMS

If the rate of attainment of phase equilibrium is determined by diffusion, mass transfer by such processes is described by the well known Fick's law[33]

$$I = -D\frac{dc}{dx} \qquad (11)$$

in which I (g cm^{-2} s^{-1}) is the material flux, D (cm^2 s^{-1}) the diffusion coefficient, and dc/dx (g cm^{-4}) the concentration gradient. For binary systems the main process is interdiffusion, which is governed by the coefficient D_v. Analysis based on the thermodynamics of irreversible processes shows that the rate of mass transfer in a multicomponent system depends on the chemical potential gradient of each component[34,35]. The relation between the interdiffusion coefficient and the thermodynamic properties of the system is given by the equation

$$D_v = D_i^* \frac{d\ln a_i}{d\ln \varphi_i} = D_i^* \frac{\varphi_i}{RT}\frac{d\mu_i}{d\varphi_i} \qquad (12)$$

where D_i^* is the self-diffusion coefficient of the ith component a_i its activity, and ϕ_i its volume fraction. The self-diffusion coefficient characterises the thermal mobility of the component molecules and is independent of the chemical potential gradient. The specific form of the composition dependence of the interdiffusion coefficient can be obtained by substituting in (12) expressions for the chemical potentials of solvent and polymer in the solution[36]:

$$D_v = D_1^*[1-(1-1/m)\varphi_1 - 2\chi\varphi_1\varphi_2] \qquad (13)$$

$$D_v = D_2^*[1-(1-m)\varphi_2 - 2m\chi\varphi_1\varphi_2]\,. \qquad (14)$$

To the approximation $m \to \infty$ Eqn. (13) becomes

$$D_v/\varphi_2 = D_1 = D_1^*(1-2\chi\varphi_1) \qquad (15)$$

where D_1 is the relative diffusion coefficient. By means of this formula the dependence of χ on mixture composition is calculated from the concentration dependence of D_1 and D_1^*.

Interdiffusion coefficients are usually determined by an optical-wedge method[37]. Analysis of the component concentration distribution curves with respect to distance by the Matano–Boltzmann method gives a solution of the Fick equation describing a non-stationary diffusion process:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_v\frac{\partial c}{\partial x}\right)\,. \qquad (16)$$

Self-diffusion coefficients are calculated by means of the modified Fujita equation[36]

$$\lg\frac{D_{1,\varphi}^*}{D_{1,0}^*} = \lg\frac{D_{1,1}^*}{D_{1,0}^*} - \frac{\beta f_1\varphi_1}{f_2+\beta\varphi_1} \qquad (17)$$

in which $D_{1,\phi}^*$, $D_{1,0}^*$, and $D_{1,1}^*$ are respectively the self-diffusion coefficient at various ϕ values, the extrapolated value of $D_{1,\phi}$ as $\phi_1 \to 0$, and the self-diffusion coefficient of the solvent, $\beta = f_1 - f_2$, and f_1 and f_2 are the fractional free volumes of solvent and polymer respectively. The last two quantities can be found from the temperature dependence of viscosity by means of Doolittle's equation[38]; $D_{1,1}^*$ is usually

determined independently by means of the Einstein-Stokes equation or by the spin-echo method[39,40].

This approach has been used in calculating thermodynamic functions of mixing of the components for an epoxide oligomer-oligomeric rubber system[41]. The observed composition dependence of interdiffusion coefficients for binary epoxide–rubber systems show (Fig.3) that the absolute value of the coefficient increases with the thermodynamic affinity between the components. At temperatures remote from the critical, as in the Ed-20-SKN-14KKG and ED-20-SKN-40KKG systems, the dependence of D_ν on mixture composition is monotonic.

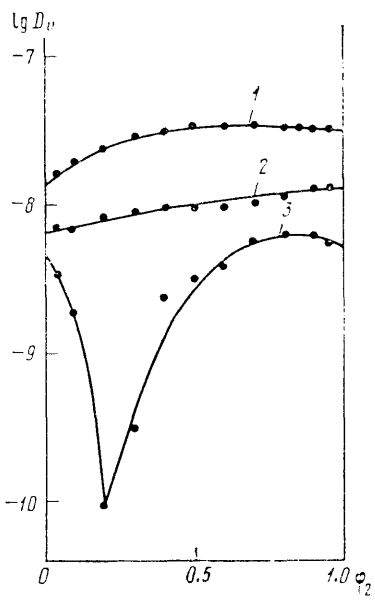


Figure 3. Concentration dependence[41] of interdiffusion coefficient of components at 70 °C in systems comprising ED-20 with different rubbers: *1*) SKN-40KKG; *2*) SKN-14KKG; *3*) SKN-8KGG.

For the ED-20-SKN-8KKG system, which separates into layers at 70 °C (Fig.1), the concentration dependence is characterised by a sharp minimum (Fig.3) in the region of critical compositions. The appearance of such minima is usually attributed to a contribution to the interdiffusion coefficient by a thermodynamic factor (Eqn.12), which tends to zero in the vicinity of the binodal[42]. The coefficient is indeed larger and greater the difference in concentration between the coexisting phases, but such difference is absent at the consolute point[7]. The depth of the extremum diminishes with rise in temperature, and at 130 °C the concentration dependence of χ becomes monotonic.

The plots in Fig.4 show a quite definite concentration dependence of χ calculated by means of Eqn.(16) for epoxide–rubber systems. It is most marked for the ED-20-SKN-8KKG system, which is characterised by the least thermodynamic affinity between the components. A similar effect of the thermodynamic nature of the components on such dependence was found experimentally for solutions of polymers[10,16,17]. With increased content of oligomeric rubber in a binary system with an epoxide the value of χ increases monotonically. An exception is the above ED-20–SKN-8KKG system, curves for which show a clear minimum ($\phi_2 = 0.2$–0.4). The quantity $\partial^2 G_{mix}/\partial\phi_2^2 > 0$ at all mixture compositions in the region of unrestricted miscibility and vanishes at the consolute point[7], and its extremal variation can be assumed to extend over a certain temperature range close to this point. The observed concentration dependence of χ is probably due to this circumstance. In general, one reason for the composition dependence of χ is the formation of association complexes of the solvent in the polymer phase[43,44].

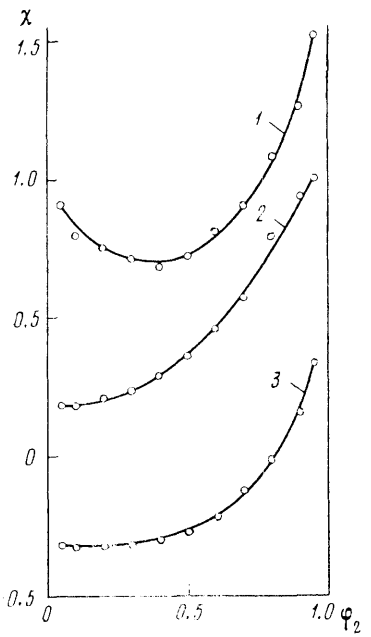


Figure 4. Concentration dependence[41] at 100 °C of χ in binary systems of ED-20 with different rubbers: *1*) SKN-8KKG; *2*) SKN-14KKG; *3*) SKN-40KKG.

Calculation disregarding the concentration dependence(9) for the ED-20-SKN-8KKG system with $(\phi_2)_{cons} = 0.24$ at $T_{cons} = 70$ °C gave $\chi_{cons} = 0.82$. Use of Eqn.(16) for the same conditions gives 0.88, which can be regarded as a more reliable value, since it is almost identical with that (0.87) predicted on the basis of the Flory-Huggins theory (Eqn.5). Calculation by means of a binodal equation apparently gives information on the mean interaction parameter of the components. This method can be usefully applied to estimate χ for systems with similar thermodynamic affinities of the components and in calculations of a spinodal.

We have used isoconcentration curves of the temperature dependence of χ to calculate thermodynamic parameters of mixing for the epoxide–rubber systems investigated[41]. The dependence on the reciprocal of the temperature is linear for all compositions, and the temperature coefficient usually increases with the volume fraction of the rubber. From the results molar thermodynamic functions of mixing were calculated for the epoxide–rubber systems by means of Eqn.(2). Results for the systems formed by ED-20 with SKN-8KKG and SKN-40KKG at 100 °C show that the function ΔG_{mix} is negative throughout the composition range (Fig.5). However, the curves differ in character: for the latter system the ΔG_{mix}–ϕ_2 curve (Fig.5*b*, curve 4) is concave

$(\partial^2 G_{mix}/\partial\phi_2^2 > 0)$, which means that the system is thermodynamically stable with respect to phase separation; from the corresponding dependence it can be concluded that the former system is considerably less stable thermodynamically. Indeed, with fall in temperature the ΔG_{mix} curves exhibit a tendency to form a convex segment, which is characteristic of systems having limited mutual solubility. Similar results have been obtained[18,19] for the ED-20–SKN-10 and ED-20–SKN-18 systems, which were regarded as having restricted compatibility. The positive enthalpies ΔH_{mix} (Fig.5) indicate that mixing is endothermic, and dissolution is due to the positive values of $T\Delta S_{mix}$ exceeding those of ΔH_{mix}. As complied above, the entropy of mixing comprises combinatorial and non-combinatorial components. Estimates showed these quantities to be comparable for the systems investigated (maximum difference between them not exceeding 50%), for which reason it is completely unjustified to ignore the non-combinatorial contribution to the entropy ΔS_{mix}.

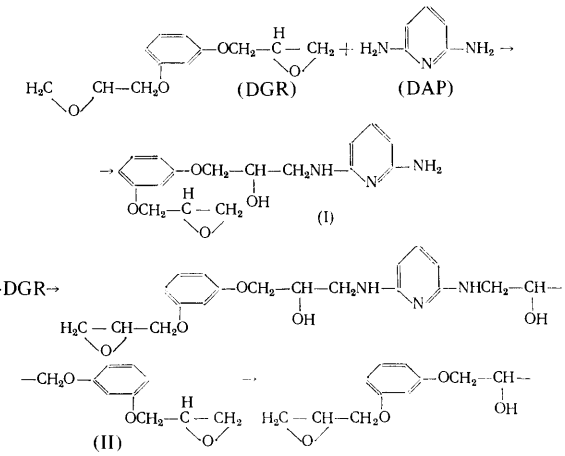
Analysis of the results obtained for all the systems investigated indicates that increase in the thermodynamic affinity between the components due to growth in polarity of the oligomeric rubber increases the absolute values of the free energy ΔG_{mix}, mainly as a consequence of decrease in the enthalpy ΔH_{mix} (Fig.5). For the system with the greatest solubility of the components (ED-20–SKN-40KKG) the enthalpy $\Delta H_{mix} = T\Delta S_{noncomb}$. Mixing under these conditions is due to the combinatorial component $T\Delta S_{comb}$: i.e. the system can be regarded as quasi-ideal.

Thus certain general conclusions can be drawn from the examination of phase equilibria and interdiffusion in the initial epoxide–rubber systems. The Flory–Huggins theory taking into account the non-combinatorial entropy component χ provides an explanation of the dependence of solubility on the thermodynamic affinity between the components.

The thermodynamic stability of the initial systems can be assessed from the quantitative relations between their kinetic and thermodynamic properties.

IV. PHASE EQUILIBRIUM AND INTERDIFFUSION DURING SETTING

The phase state established when the components are mixed undergoes significant changes during the chemical reaction. The reason is a continuous change in the chemical nature of the epoxide component, evident in variation in its thermodynamic properties and increase in the molecular mass:



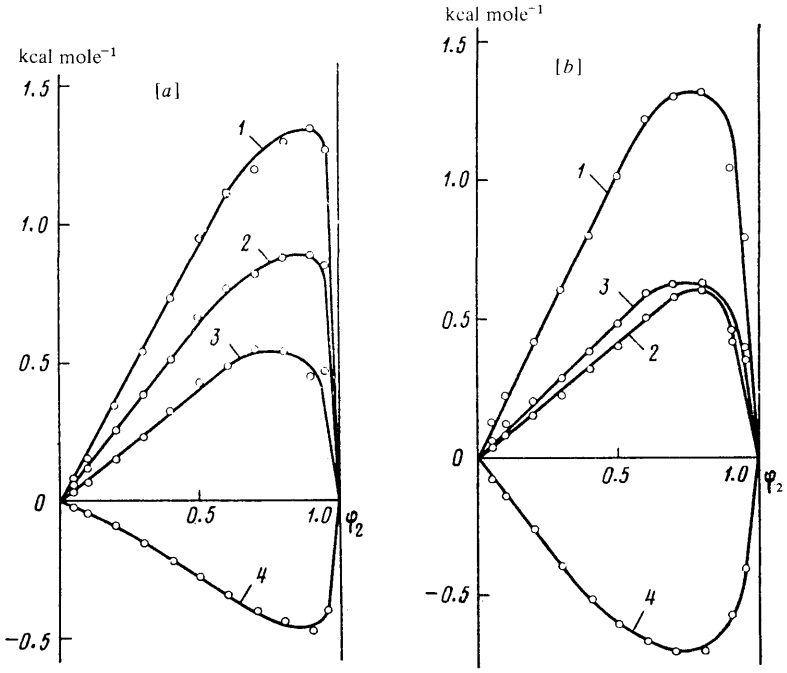
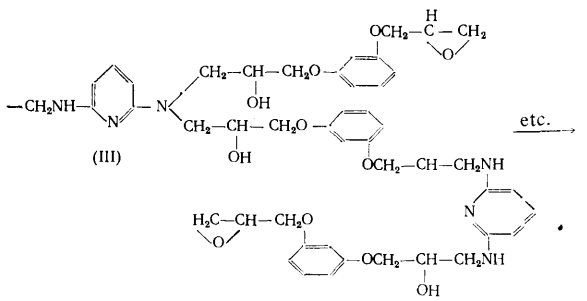


Figure 5. Concentration dependence[41] at 100 °C in binary systems of ED-20 with: *a*) SKN-8KKG; *b*) SKN-40KKG for thermodynamic functions of mixing: *1*) $T\Delta S_{mix}$; *2*) ΔH_{mix}; *3*) $T\Delta S_{mix,non\text{-}comb}$; *4*) ΔG_{mix}.



Phase equilibrium and diffusion during the three-dimensional polycondensation of an epoxide have been investigated on epoxide–rubber systems based on the diglycidyl ether of resorcinol (DGR) and oligomeric rubbers varying in chemical nature[45]. The hardener used was 2,6-diaminopyridine (DAP).

Additive calculation of the solubility parameters of the chemical conversion products of an epoxide oligomer showed[45] that they remain almost unchanged up to high degrees of converson. However, increase in the number of hydroxy-groups in the epoxide component during the reaction favours specific interactions in the setting system. The presence of such interactions and the increase in molecular mass of the epoxide are probably responsible for the change in phase state during the reaction. The character of the phase equilibrium and the rate of its attainment at different stages in the hardening of the epoxide can be assumed to be the main factors determining the mechanism of structure formation.

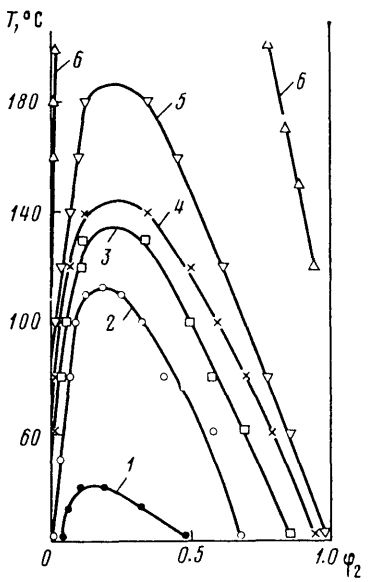
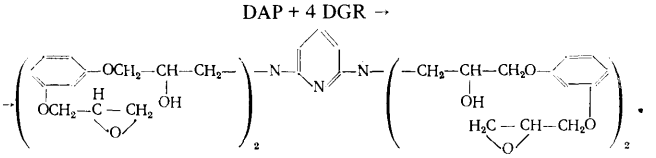


Figure 6. Phase equilibrium diagrams[45] of (DGR-DAP)–PEF-3A system for different degrees of conversion (%): *1*) 31; *2*) 37; *3*) 40; *4*) 42; *5*) 44; *6*) 53.

Analysis of the position of the binodals in the epoxide–rubber system at the stage of mixing of the components shows that increase in the thermodynamic affinity of the rubber for the epoxide in the sequence SKN-8KKG < SKN-14KKG < PEF-3A leads to expansion of the region of homogeneous mixing, in agreement with earlier results. Change in phase equilibrium during chemical reaction was studied on model systems representing products of the hardening of diglycidyloxybenzene by various quantities of pyridinediamine that are completely consumed:



The model systems adopted—DGR + (IV)—are not adequate, of course, to describe the actual products of hardening (I–III) and can be regarded merely as qualitative analogues of the real systems, employed for the phenomenological description of the change in phase state under the influence of chemical reaction.

Polycondensation of the epoxide oligomer is accompanied by expansion of the region of phase separation (Fig. 6); the solubility curves shift to higher temperatures, and the solubility of the components becomes infinitesimal when a certain degree of chemical conversion of the epoxide is reached. Analysis of the results revealed a relation between the initial compatibility (i.e. before the start of reaction) and the rate of change of miscibility during reaction. Breakdown of the stability of the epoxide solution in the setting system takes place at different stages of chemical conversion of the epoxide depending on the initial compatibility. As a consequence, change in the phase state of the system occurs at different rates of conversion of the epoxide (Fig. 7).

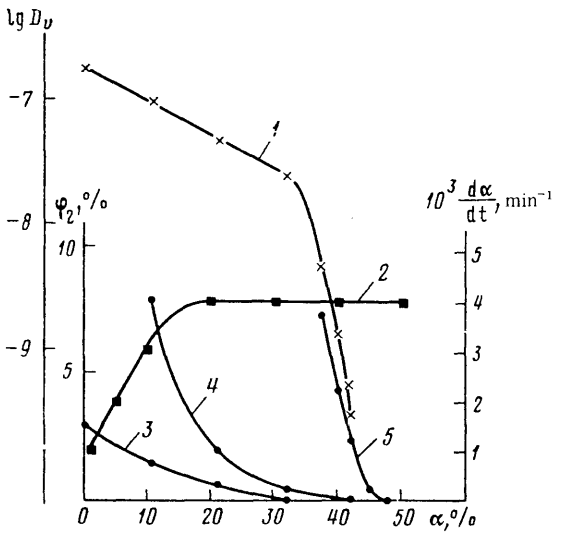


Figure 7. Variation[45] of parameters during hardening at 90 °C in binary systems of DGR–DAP with different rubbers: *1*) interdiffusion coefficient, PEF-3A; *2*) rate of reaction, PEF-3A; 3) solubility of SKN-8KKG; 4) solubility of SKN-14KKG; 5) solubility of PEF-3A.

Fig. 8 illustrates the temperature dependence of the interaction parameter calculated from the binodal equation for the (DGR-DAP)–PEF-3A system. A significant difference in the type of dependence is evident for systems at the stages of

mixing of the components and of chemical conversion of the epoxide. The dependence of the enthalpy of mixing (the temperature coefficient of χ) over a wide temperature range evident in the latter case cannot be explained by ignoring the concentration dependence of χ, since averaging χ with respect to composition leads to its linear dependence on the reciprocal of the temperature, as shown earlier on binary systems. The reason for the anomalous behaviour of setting systems must most probably be sought in their tendency to develop specific interactions. The increase in the enthalpy of mixing as the temperature is lowered suggests that the predominant form of specific interaction is association of oligomeric epoxide molecules, which ultimately impedes mutual dissolution.

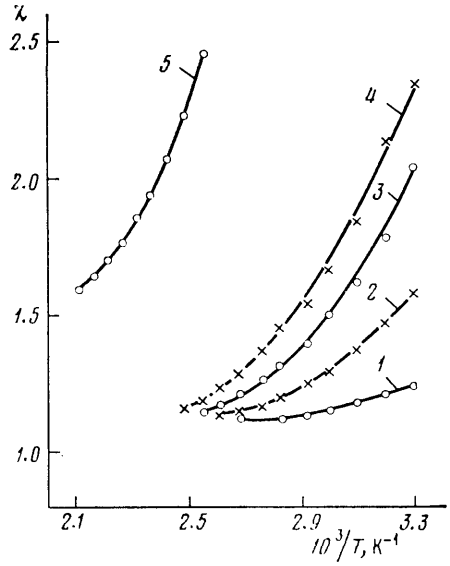


Figure 8. Temperature dependence[46] of χ in (DGR-DAP)–PEF-3A system at different degrees of conversion (%): *1*) 37; *2*) 40; *4*) 44; *5*) 53.

The diffusion method described previously[36] has been used to determine thermodynamic functions of mixing in a hardening epoxide–rubber system of type (DGR-DAP)–PEF-3A. The character of the concentration dependence of the interdiffusion coefficient is found experimentally to change during the course of polycondensation of the epoxide oligomer, from a monotonically increasing to a non-monotonic function of composition with a break in the region of two-phase mixtures[46]. Analogous results have been obtained in a study of diffusion in systems formed by an epoxide oligomer with a hardener and with a plasticiser[47]. The appearance of minima and breaks on the concentration curves during the chemical conversion of the epoxide is due to diminution in the mutual solubility of the components and separation of the hardening system into layers.

The concentration dependence of the interaction parameter calculated by means of Eqn.(16) for such systems with different degrees of hardening of the epoxide oligomer is qualitatively the same as the corresponding dependence at the mixing stage. It is more marked for a system containing the epoxide oligomer at a higher degree of conversion, which is consistent with the hypothetical formation of molecular association complexes of the solvent in the polymer phase[43,44].

The dependence of the interaction parameter on the reciprocal of the temperature is linear over the range 90–130 °C whatever the proportions of the hardening epoxide oligomer and the rubber[46]. As with the initial systems, the temperature coefficient increases with the proportion of the rubber. Its absolute value at a constant volume fraction of the rubber is almost independent of the degree of conversion of the epoxide oligomer. Molar thermodynamic functions have been calculated for mixing the rubber PEF-3A with epoxide oligomers of different degrees of chemical conversion. The changes in chemical potential of both components decrease in absolute magnitude during the chemical reaction: i.e. the thermodynamic affinity of the components diminishes. A consequence is a decrease in the absolute magnitude of the molar free energy of mixing (Fig. 9).

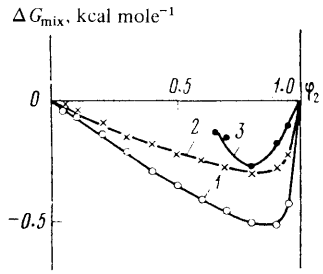


Figure 9. Concentration dependence[46] of ΔG_{mix} in (DGR-DAP)–PEF-3A system at 90 °C for different degrees of conversion (%): *1*) 0; *2*) 21; *3*) 42.

Analysis of the results[46] has shown that the solubility remains endothermic in character during hardening of the epoxide oligomer, with the enthalpy of mixing little changed. This means that the change in free energy of mixing during the reaction is due mainly to the entropy factor. For the initial systems the change in free energy has been determined predominantly by the enthalpy component. The entropy of mixing in turn changes during hardening of the system mainly because of the non-combinatorial term. From this it can be concluded that over the temperature range investigated the hardening system exhibits a tendency to form a solution having a more ordered arrangement of the molecules.

Thus study of phase equilibrium and interdiffusion during hardening of an epoxide–rubber system has shown that the Flory–Huggins theory describes satisfactorily the thermodynamics of the process only over a narrow temperature range. The thermodynamic stability of a solution of an oligomeric rubber in a hardening epoxide oligomer is determined mainly by the entropy factor. The role of specific interactions becomes greater with hardening of the epoxide.

V. MECHANISM OF FORMATION OF PHASE STRUCTURE

The mechanism of phase separation is determined by the relative rates of transition of the system into a non-equilibrium state w_{neq} and for structural relaxation w_{sr}.[48] When $w_{neq} < w_{sr}$, heterophase fluctuations increase with time while remaining unchanged with respect to composition: i.e. the system comprises two phases from the very start. Such a mechanism of phase separation is termed *nucleation*. When $w_{neq} > w_{sr}$, the system stratifies by a spinodal mechanism without formation of heterophase nuclei. For a long time,

right until phase separation, the structure comprises a single phase with fluctuations of composition, which increase with time. A characteristic feature of structures formed by spinodal stratification is the spatial coherence of each phase and the absence of isolated inclusions. Such a mechanism of phase separation is observed comparatively rarely and has been little studied hitherto. Separation by a nucleation mechanism has been studied in greater detail[10,49-98]. Generation of particles of a new phase (nucleation) can take place homogeneously (within a single phase), heterogeneously (e.g. on the surface of the vessel or trace impurities[53-55]), and also by "self-nucleation"[56-59].

The first theories of the homogeneous formation of nuclei[60-63] were based on the postulate that the factor governing nucleation is the relative supersaturation $\Pi = c_{sup}/c_{sat}$, the ratio of the concentrations of supersaturated and saturated solutions. The rate of nucleation is related to the supersaturation by the formula

$$w_{nu} = K_1 \exp[-K_2/(\ln\Pi)^2] \qquad (18)$$

in which K_1 and K_2 are constants. In view of the strong dependence of the rate on the supersaturation it was suggested[62,63] that a critical supersaturation Π_{cr} existed, below which the rate of formation of nuclei was so small that it could be neglected, i.e. $w_{nu} = 0$. Supersaturation is necessary to accumulate the energy required to surmount the barrier ΔG_{nu} associated with formation of nuclei (creation of an interface). The maximum free energy ΔG_{nu} corresponds to the critical size below which a nucleus cannot grow.

Theories of homogeneous nucleation were subsequently improved[64-67]. The rate of generation of a new phase in a condensed system was shown to depend not only on the degree of supersaturation but also on the rate of diffusion of material through the interface. For example, the rate of generation of crystals is described by the equation[67]

$$w_{nu} = (NkT/h)\exp[-(\Delta G_{nu} + \Delta G_D)/kT] \qquad (19)$$

in which N is the number of molecules in 1 cm^3 of liquid, k Boltzmann's constant, h Planck's constant, and ΔG_D the activation free energy of diffusion. The principles underlying the theories of homogeneous nucleation were used to develop theories of heterogeneous nucleation and "self-nucleation" of a new phase. The kinetics and the mechanism of growth of the nuclei have been investigated in greatest detail for crystallisation[64,68-73]. The development of isothermal crystallisation can be expressed[71-73] by the formula

$$a_t = 1 - \exp(-Kt^n) \qquad (20)$$

where a_t is the fraction of the material that has crystallised by time t, and K and n are constants. The rate of growth of a phase structure in a viscous condensed system is proportional to the diffusion coefficient D and the concentration gradient dc/dx resulting from supersaturation[74]:

$$w_{gr} \sim D\frac{dc}{dx} . \qquad (21)$$

The total rate of formation of the new phase is determined by the rate of nucleation and the rate of particle growth[74]:

$$w_{ph} = w_{nu} w_{gr}^n . \qquad (22)$$

Such are the general laws of formation of a new phase in various heterophase systems.

In real heterophase polymer systems, which are of the greatest interest, chemical reaction and phase separation often take place in some measure simultaneously, and exert a strong mutual influence. We shall examine some examples of such processes. Heterophase polymerisation processes of dispersion[75], suspension[76], emulsion[10,77-79], and precipitation[80-87] types have been investigated in some detail.

The main conclusion from the diffusion theory of dispersion polymerisation[75] has been the relation

$$w_{nu} = w_{init}[1 - \pi r^2 N (2P_{cr}D/K_p[M])^{1/2}] \qquad (23)$$

where w_{init} is the rate of initiation, r the particle radius, N the number of particles in unit volume, P_{cr} the critical degree of polymerisation necessary for nucleation of the growing macroradical, D the mean diffusion coefficient for the growing radical, k_p the polymerisation rate constant, and [M] the monomer concentration. The equation for the critical degree of polymerisation relates the final number of particles formed to the solubility of the polymer, dissolving power of the medium, and the critical relative supersaturation:

$$P_{cr} = -\ln\varphi_p \Big/ \left(\chi - 1 - \frac{v_0}{v_m}\ln\Pi_{cr}\right) \qquad (24)$$

with ϕ_p the fraction by volume of the polymer, v_0 the molar volume of a monomer unit, and v_m the molar volume of the solution. Other theoretical approaches have been made to the description of dispersion polymerisation, but none gives more than a qualitative explanation of the observed relations between particle size, polymer solubility, dissolving power of the medium, and quantity of stabiliser.

The simple relation

$$w_p = K_p(N/2)[M] \qquad (25)$$

was established[78] for the dependence of rate of emulsion polymerisation on number of particles. It was subsequently found that this equation provides a satisfactory description of the polymerisation only of those monomers that dissolve their own polymers, e.g. styrene, butadiene, isoprene. The emulsion polymerisation of vinyl chloride and acrylonitrile, which do not dissolve their own polymers, takes place on the surface of particles, not within them. These processes are described in terms of the theory of Medvedev and Sheinker[79], according to which the rate of polymerisation is proportional to the total particle surface. Furthermore, neither theory[78,79] has proved applicable to the emulsion polymerisation of ethylene and vinyl acetate.

Precipitation polymerisation may be accompanied by crystallisation of the polymer[64,88]. The resulting crystals then have a special morphology (fibrillar and acicular), and their macromolecules have extended conformations. Crystallisation in turn influences polymerisation, changing its rate and mechanism.

The copolymerisation of styrene with rubber in bulk or in the block-suspension modification merits separate consideration[84]. The resulting copolymers have a peculiar phase structure: rubber particles surrounded by a thin film of grafted butadiene–styrene copolymer are dispersed in a polystyrene matrix; the particles are inhomogeneous, containing a large quantity of occluded polystyrene as still finer inclusions. The polystyrene particles are occluded by the rubber phase at the moment of phase inversion (occlusion of the first kind) and also during further copolymerisation by separation from the rubber phase of the polystyrene formed (occlusion of the second kind).

A special case of phase separation is observed in the formation of a network structure by polymers[89]. This phenomenon, which has been studied in detail by Dusek[90-93], has been termed *microsyneresis*. It is evident in the separation of liquid (solvent, monomer, oligomers) from swollen cross-linked macromolecules as a consequence of diminution in their swellability due to intramolecular cross-linking of the macromolecules in the course of three-dimensional polymerisation. To describe the thermodynamics of microsyneresis Dusek started from the equation

$$\mu_i - \mu_i^0 = (\Delta\mu_i)_{mix} + RTv_i\left[\varphi_p^{1/3}\frac{\langle r^2\rangle_d}{\langle r^2\rangle_{sw}} - \frac{1}{2}\varphi_p\right] \qquad (26)$$

in which μ_i and μ_i^0 are the chemical potentials of swollen and unswollen polymers respectively, $(\Delta\mu_i)_{mix}$ is the change in chemical potential of the polymer on mixing, ν is the concentration of elastically active chains, v_i is the molar volume of the solvent, ϕ_p is the fraction by volume of the polymer, and $\langle r^2\rangle_d$ and $\langle r^2\rangle_{sw}$ are the mean square distances between the ends of the network in dry and swollen polymers respectively. Dusek took into account also the variation in entropy of mixing and in chain distribution with degree of swelling. Substitution in Eqn.(26) for $(\Delta\mu_i)_{mix}$ from the Flory-Huggins theory (2) yields a condition of phase separation depending on χ and ν. Hence there should exist critical values of χ and ν on attaining which (in the course of three-dimensional polymerisation) the system begins to stratify. In spite of the availability of experimental results consistent with the theoretical calculations, the legitimacy of the postulates made by Dusek in the calculations is open to doubt[89]. This arises from disagreements concerning the form of the elastic potential[94,95], and also to the absence under real conditions of the proportionality between the dimensions of the network during swelling and the volume of solvent absorbed that is assumed in the calculations.

Thus formation of a new phase complicated by chemical reaction is difficult to describe quantitatively. Existing theories of these processes have not yet reached a stage of development at which a clear physicochemical model could be used to predict the number, size, and shape of the particles formed under any specified conditions.

Table 2. Degrees of conversion α_{sep} at which phase separation begins in (DGR-DAP)-rubber systems[98].

Rubber (%)	PEF-3A (0,2)	PEF-3A (0,5)	PEF-3A (1,0)	PEF-3A (3,0)	PEF-3A (5,0)	SKN-8KKG (0,1)	SKN-8KKG (0,2)	SKN-14KKG (0,2)
α_{sep}*	0.46	0.45	0.44	0.42	0.39	0.30	0.30	0.39
α_{sep}**	0.50	0.49	0.46	0.43	0.41	0.41	0.39	0.46

* Determined from phase equilibrium diagrams.
** Determined from light-scattering data.

Investigation of the formation of a phase structure in epoxide–rubber systems began quite recently[45,98]. Views on the mechanism for a heterophase polymer system were based on results for the phase equilibrium, interdiffusion of components, and kinetics of particle growth of the disperse phase. The scattering of light[99] and the turbidity spectrum[100] were used to examine the kinetics. The phase structure of a hardened system has been studied by electron microscopy[101]. The start of phase separation in the hardening system was established from the kinetic curves of light-scattering intensity. Comparison of these results with Fig.7 revealed that phase breakdown takes place at a later stage than would follow from the phase equilibrium diagram (Table 2). The difference may be due to inadequacy of the model for the real system, but also may have thermodynamic causes. Chemical conversion of the epoxide oligomer disturbs the condition of thermodynamic stability of the solution, corresponding on the phase equilibrium diagram to passage of the binodal through a point determined by the concentration adopted and the hardening temperature. However, separation of heterophase particles begins not at the solution composition corresponding to the limiting solubility of the components but on the attainment of some critical degree of supersaturation.

The variation in mean particle size of the disperse rubber phase during hardening, indicated by the turbidity spectrum, is extremal (Fig.10). The observed course of the kinetic curves can be attributed to the appearance at a certain instant of a fraction of smaller particles.

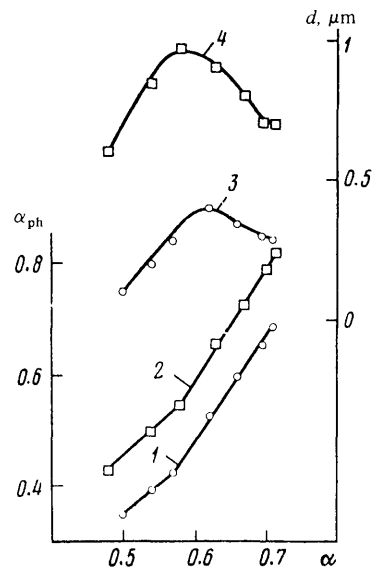


Figure 10. Dependence at 90 °C [98] of degree of phase conversion and mean particle size of disperse phase on extent of chemical reaction for the (DGR-DAP)–PEF-3A system containing different initial rubber contents (%): *1*) conversion (0.5); *2*) conversion (1.0); *3*) particle size (0.5); *4*) particle size (1.0).

Comparison of the particle-size distribution curves for the disperse rubber phase in the hardened systems with the phase diagrams at the mixing stage (Fig.11) indicates that the structure of the hardened composition is related to the compatibility of the initial components. Indeed, the rubber SKN-8KKG, which is poorly compatible with the epoxide oligomer, has the widest particle-size distribution. The use of systems that are most remote from the consolute temperatures, e.g. EO–PEF-3A, narrows the distribution significantly. All the compositions investigated have a bimodal particle-size distribution of the disperse phase. The bimodal character is retained with increase in the volume fraction of the oligomeric rubber. The ratio between coarse and fine particles changes: the mean particle size increases.

The peculiarities of the phase structure of a hardened modified composition—the presence of discrete, spatially unconnected rubber particles dispersed in an epoxide matrix—indicate a nucleation mechanism of heterophase formation. The passage of the particle-size distribution curve of the rubber phase through two maxima apparently indicates a two-stage formation of the phase structure.

Analysis of the results suggests a mechanism of formation of a two-phase structure in a hardening epoxide–rubber system with two stages—nucleation of a new phase and its subsequent growth—involved in transition to a non-equilibrium

state. The rate of growth of nuclei is determined by a parameter equal to the product of the interdiffusion coefficient and the concentration gradient. This gradient is in turn related to the degree of supersaturation of the solution, which is proportional to the rate of chemical reaction of the epoxide oligomer. Fig.7 illustrates the experimental variation in rate of chemical conversion and in interdiffusion coefficient of the components with the degree of conversion of the epoxide. Since this coefficient and the concentration gradient vary in opposite senses, the rate of growth of nuclei is an extremal function of duration of hardening. At the start of the process particle growth is limited by the rate of chemical reaction.

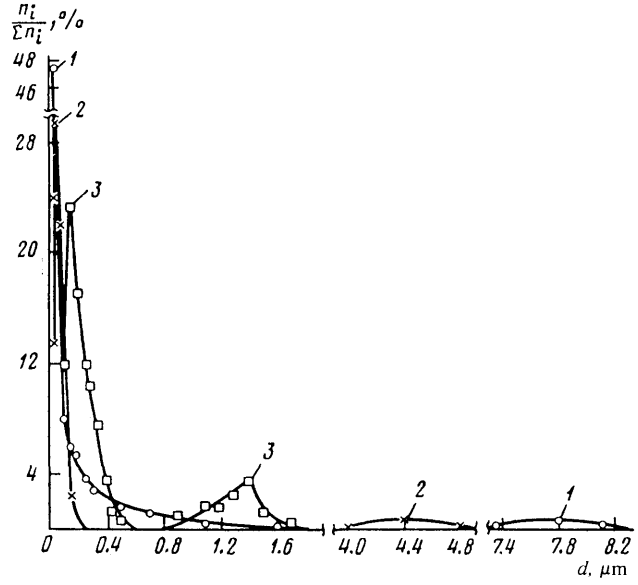


Figure 11. Particle-size distribution curves[45] of disperse phase in hardened systems comprising DGR-DAP with different rubbers: *1*) SKN-8KKG; *2*) SKN-14KKG; *3*) PEF-3A.

The compatibility of the components of an epoxide—rubber system determines the time at which nucleation of a new phase begins (Fig.7). If primary nucleation takes place at a stage limited by the concentration gradient dc/dx, the increase in supersaturation of the solution during polycondensation of the epoxide oligomer is balanced by diffusion in the direction of the centre of growth. A feature of this stage is the coarsening of heterophase particles by "diffusion consumption" of finer particles. Compensation of supersaturation breaks down at a stage determined by the interdiffusion coefficient: as the latter decreases, the radius of the diffusion sphere around the growth centre diminishes. A consequence is the appearance and growth at the periphery of this sphere of regions of localised supersaturation, in which formation of new growth centres—secondary nucleation—results from further chemical change. A mechanism of two-stage nucleation is confirmed by the kinetics of particle growth of the disperse rubber phase. Decrease in the mean heterophase particle diameter is apparently also due to secondary nucleation (Fig.10).

Two-stage formation of the phase structure is evident also in the variation in number of heterophase particles during hardening. The first stage involves a sharp drop in the number as a consequence of intense "diffusion consumption" of extremely fine particles. Increase in the number of particles of the disperse phase at the second stage is due to secondary nucleation. This may be due to diminution in the ability of the cross-linked macromolecules to swell during three-dimensional polycondensation, by analogy with microsyneresis[97]. This hypothesis is supported[98] by the experimental dependence of degree of phase conversion on extent of chemical reaction in the system (Fig.10). Breaks in the curves occur in the region of a critical extent of chemical conversion ($\alpha_{cr} \approx 0.58$):[102] i.e. secondary nucleation begins in the region of gel formation.

The suggested mechanism of structure formation enables us to elucidate the type of relation between the thermodynamic compatibility of the components and the phase structure of the hardened modified compositions. The particle size of the disperse phase is determined by the rate and the duration of growth. The free energy of mixing of the initial epoxide—rubber system determines the "reserve" of thermodynamic stability of the solution towards separation into layers. The greater the affinity between the components the longer the life of the hardening solution and the later does the first nucleation take place: i.e. increase in the compatibility of the components leads to a shortening of growth time and hence a decrease in particle size at the first stage. The size of the particles separating after the first nucleation (second peak in the particle-size distribution curves of the heterophase—Fig.11) does indeed diminish with increase in compatibility. Furthermore, a high degree of supersaturation in systems of well miscible components leads to earlier onset of diffusion control. As a result, both the rate and the time of growth of particles of the disperse phase that separate after the second nucleation (first peak on the distribution curves) increase. Hence the particle-size distribution of the disperse phase becomes narrower with increase in thermodynamic affinity between the components.

Thus the remoteness of the system from the consolute temperature affects the evolution of phase transitions and ultimately determines the character of the phase structure.

VI. CONCLUSION

The laws of structure formation established in this Review enable certain conclusions to be drawn on possible ways of controlling the phase structure. Among factors determining the latter are the thermodynamic properties of the components and the conditions of hardening of epoxide-rubber systems.

Increasing the thermodynamic affinity between the components may effect a narrower particle-size distribution of the disperse phase. In the limit, with systems having components of high miscibility, the solution may remain stable up to the point of gelation. Two-stage formation of the phase structure will then become a single-stage process, with a consequent unimodal particle-size distribution of the heterophase. In this case the particle size diminishes when the components are more compatible[6]. By combining components differing in chemical nature and also varying their molecular masses it is possible to regulate between wide limits the mean particle size and polydispersity of the rubber in the hardened systems. It is noteworthy that the mean size and the polydispersity of the heterophase particles are related in such a way that increase in one of them leads to an increase in the other, and conversely.

Varying the temperature conditions of hardening has a more complicated influence on the mechanism of structure formation. Raising the reaction temperature both increases the rate and shortens the time of particle growth. The particle size of phase inclusions is determined by the influence of temperature on each of these factors, so that the temperature dependence of the particle size of the rubber should be extremal.

With rise in reaction temperature the primary nucleation takes place at a higher degree of conversion. The time at which secondary nucleation begins depends on the ratio of the activation energies of chemical reaction and diffusion. Thus with rise in temperature the two successive nucleations must be expected to approach each other in degree of conversion, as a result of which the polydispersity of the particles should diminish. If it is assumed that secondary nucleation is associated with gel formation, change in the reaction temperature should not displace the start of diffusion control. The polydispersity will then be less dependent on temperature.

Change in the functionality of the initial oligomers has a significant influence on the critical extent of conversion, which constitutes yet another factor affecting polydispersity. Increasing the rubber concentration leads to an increase in the mean particle size of the disperse phase without significant change in polydispersity. Thus the most effective method for regulating the particle size and polydispersity of the rubber during hardening of an epoxide–rubber system is to vary the chemical nature of the components.

Research on heterophase polymer compositions should be aimed at establishing a quantitative theory of formation of the phase structure, which will contribute to a deeper insight into the relation between the chemical nature of the initial components and the phase structure of the polymer compositions. On the basis of the quantitative relations between these factors it will become possible to control the physicomechanical properties of the multicomponent materials, which will lead to further progress in this promising field of polymer science.

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Natural Xanthones

O.A.Denisova-Dyatlova and V.I.Glyzin

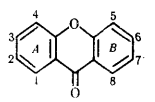
The available information on the abundance of natural xanthones in nature and the methods for the determination of their structure, biogenesis, and pharmacological properties is surveyed and described systematically.
The bibliography includes 151 references.

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I. INTRODUCTION

The term "xanthone" denotes a chemical compound with the dibenzo-γ-pyrone structure:



The unsubstituted xanthone has not been discovered in nature but its numerous derivatives have been isolated from representatives of higher plants, lichens, and lower fungi.

The first review on natural xanthones, published in 1961,[1] describes only 17 compounds of which 11 have been detected in various parts of flowering plants, 5 are metabolic products of lower fungi, and one has been isolated from lichen species.

Eight years later Carpenter et al.[2] examined the chemotaxonomic aspect of more than 70 natural xanthones and surveyed the available information about the possible ways of their biogenesis in plants. Chemotaxonomic problems were subsequently considered in greater depth in connection with xanthones from tropical plants[3].

In 1977 Hostettmann and Wagner[4] described one of the extensive groups of natural xanthones—xanthone glycosides.

The sharp growth of interest in natural xanthones in recent years can be readily accounted for by the fact that the first studies in the field of the pharmacological properties of xanthone derivatives already indicated that compounds of this class show promise.

The enormous amount of information accumulated during the last 20 years requires a clear-cut systematic treatment as regards questions concerning primarily the qualitative composition and physicochemical and pharmacological properties of natural xanthones. The employment of synthetic chemical methods for the preparation of highly efficient medicinal agents based on natural xanthones is also of considerable interest. However, the reviews published in recent years deal mainly with problems associated with the chemotaxonomy and biogenesis of xanthones. The aim of the present review is therefore to give a systematic account of the data on the qualitative composition, the methods for the determination of structure, and the pharmacological properties of natural xanthones.

II. CLASSIFICATION OF NATURAL XANTHONES

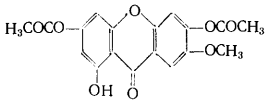
The qualitative composition of natural xanthones is extremely varied. The earlier classification of xanthones was based on the principle adopted in the classification of coumarins and chromones (derivatives of 5,6-benzo-α-pyrone and 5,6-benzo-γ-pyrone respectively).[5] However, in recent years compounds which do not fit within the framework of the proposed classification have been discovered. We believe that all the natural xanthones known at the present time should be divided into the following three groups:

1. Xanthones proper substituted by alkoxy-, alkyl, and alkenyl groups, *C*- and *O*-glycosidic residues, and chlorine atoms in positions *1—8*.
2. Pyrano- and dihydropyrano-xanthones.
3. Furano- and dihydrofurano-xanthones.

1. Xanthones Proper

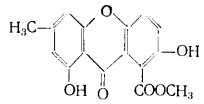
The majority of the xanthones discovered in nature are hydroxy- or methoxy-derivatives of xanthone. Tri- and tetra-substituted xanthones are most abundant. A characteristic feature of the tetrasubstituted xanthones is the presence, as a rule, of substituents in the 1- and 3-positions in the xanthone nucleus and in the main these are xanthones with substituents in the 1,3,5,8-, 1,3,7,8-, and 1,3,6,7-positions[2,4]. Pentasubstituted xanthones are encountered quite frequently. These are as a rule partly or fully methoxylated compounds containing in most instances between three and four methoxy-groups. Xanthones with one or two substituents are encountered somewhat more rarely and among the disubstituted xanthones those having substituents in the 1,5- and 1,7-positions are most abundant[3,5], Several hexasubstituted xanthones have been described. These are mainly either fully methoxylated compounds or compounds containing five methoxy-groups[5,6].

Xanthones with a greater number of substituents have not been detected in nature. Acetoxy-derivatives of xanthones are encountered in nature extremely rarely, especially among higher plants. A compound of this type [compound (I)] has been isolated from *Lawsonia inermis* (Lythraceae):[7]

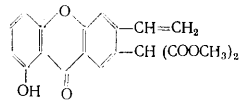


(I)

Several methoxycarbonyl derivatives of xanthone have been described. Among higher plants, *Cassia occidentalis* (Fabaceae), for example, contains methoxycarbonylxanthones (II).[8] Methoxycarbonylxanthones (III) have also been found in certain lower fungi—in the mycelium of *Mycosphaerella rosigena*:[9]

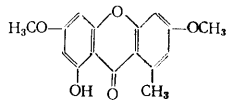


(II)

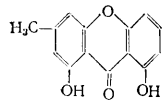


(III)

Methylated xanthones are encountered mainly in lichens, in the mycelia of certain fungi [compounds (IV)], and extremely rarely in certain higher plants [compounds (V)].[10]

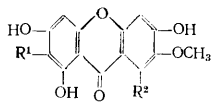


(IV)



(V)

Xanthones containing the isopropenyl group constitute a fairly extensive set of compounds distributed mainly among plants of the family Guttiferae [structures of type (VI, a and b)].[2,3,5] Substituents with a longer aliphatic chain are not characteristic of xanthones, but a xanthone containing the diene substituent geranyl has been isolated from the stems of *Garcinia cowa* (Guttiferae) [compound (VIc)]:[11]



(VI)

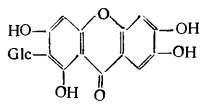
(a) R^1=H, R^2=$CH_2CH{=}C(CH_3)_2$; (b) R^1=R^2=$CH_2CH{=}C(CH_3)_2$; (c) R^1=H, R^2=geranyl.

Chloroxanthones constitute a special group among xanthones proper, since they are the products of the vital activity of lichens and have not been detected in higher plants.

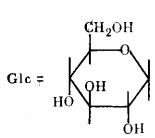
Xanthones containing in their molecule a carbohydrate substituent—xanthone glycosides—merit special attention. They can be divided into two groups: *C*-glycosides and *O*-glycosides. In contrast to the *O*-glycosides, the *C*-glycosides are resistant to acid and enzymatic hydrolysis, since the sugar component is attached to the aglycone by a C–C bond. The xanthone *C*-glycosides are encountered in nature comparatively rarely and have as a rule isotypical structures.

The aglycones of xanthone *C*-glycosides are hydroxy-derivatives of xanthone with substituents in the 1,3,6,7- or 1,3,5,6-positions in the xanthone nucleus. The carbohydrate component of the *C*-glycosides consist of glucose or glucobiose residues.

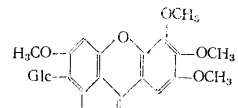
Mangiferin (VII),[12–16] which has the structure of 2-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone, is the most abundant representative of the *C*-glycosides:



(VII)

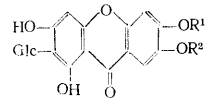


In plants mangiferin is as a rule accompanied by its isomer isomangeriferin, which has the structure of 4-*C*-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone[17]. Among the derivatives of 1,3,6,7-tetrahydroxyxanthone, the 3-methyl ether of mangeriferin[18], glucomangiferin (2-*C*-β-D-glucobiosyl-1,3,6,7-tetrahydroxyxanthone), and glucoisomangiferin (4-*C*-β-D-glucobiosyl-1,3,6,7-tetrahydroxyxanthone) have also been discovered in nature[19]. The xanthone *C*-glycosides with substituents in the 1,3,5,6-positions in the aglycones are encountered more rarely. 2-*C*-β-D-glycosyl-1,3,5,6-tetrahydroxyxanthone[20], its 5-methyl ether, called iris-xanthone, since it was first isolated from the roots of *Iris florentina* L.,[21] and its 3,5,6-trimethyl ether, obtained from *Hoppea dichotoma*,[22] have now been described. The only *C*-glycoside of a penta-substituted xanthone [compound (VIII)] known at the present time has also been isolated from *Hoppea dichotoma*:[22]



(VIII)

The discovery in nature of compounds having two carbohydrate substituents, one of which is linked to the aglycone by a C–C bond and the other by a C–O bond, made an important contribution to the study of xanthone glycosides. Thus acid hydrolysis of these compounds can yield the corresponding sugar and the *C*-glycoside. An example is provided by the *O*-glycosides of mangiferin isolated from *Gentiana asclepiadea* L. [compounds (IX) and (X)].[23]

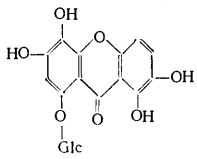


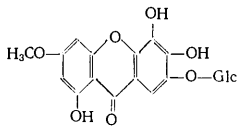
(IX) R^1=H, R^2=β-D-glucosyl;
(X) R^1-β-D-glucosyl, R^2=H.

Xanthone *O*-glycosides are encountered in plants much more frequently than the *C*-glycosides and have a more varied qualitative composition. Both *O*-monosides and *O*-biosides have been described. The monosaccharide *O*-glycosides of xanthones contain only β-D-glucose as the carbohydrate substituent[3]. Disaccharides are formed as a rule by primeverose (β-D-xylopyranosyl-β-D-glucopyranose) and rutinose (α-L-rhamnopyranosyl-β-D-glucopyranose).

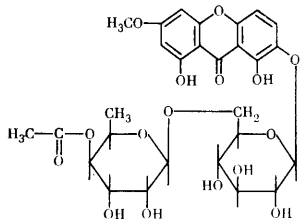
The aglycones of xanthone *O*-glycosides are tri-, tetra-, and penta-hydroxy-xanthones. The glycosides of tetra-substituted xanthones with oxygen-containing substituents in the 1,3,7,8-positions are most widely distributed. The glycosides of trihydroxyxanthones are encountered more rarely. Hitherto only two such compounds have been described in the literature: 1-hydroxy-7-methoxy-3-*O*-primeverosylxanthone, detected in the roots of the various *Gentiana* species[24], and 5-hydroxy-1-methoxy-3-*O*-rutinosylxanthone, isolated from *Canscora decussata* Schult[25]. Of the pentahydroxyxanthone glycosides, 1-*O*-β-D-glucopyranosyl-3,8-dihydroxy-4,5-dimethoxy-xanthone, detected in the leaves of *Gentiana campestris* L.,[26] 1-*O*-glucosyl-3,4,7,8-tetrahydroxyxanthone from the aerial part of *Swertia angustifolia* Buch.-Ham. [compound (XI)],[27] and 7-*O*-glycosyl-1,5,6-trihydroxy-3-methoxyxanthone from *Hoppea dichotoma* [compound (XII)] [22] have now been

described.

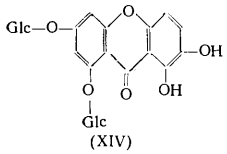

(XI)


(XII)

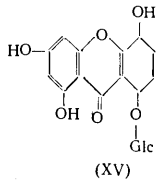
The only xanthone acyl-*O*-glycoside known hitherto, which was discovered in the leaves of *Gentiana bavarica* L.,[28] has the structure of 7-*O*-acetylrutinosyl-1,8-dihydroxy-3-methoxyxanthone (XIII).[29]


(XIII)

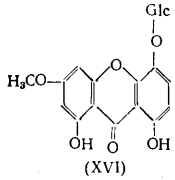
The xanthone diglucoside having the structure of 1,3-di-*O*-glucosyl-7,8-dihydroxyxanthone (XIV) was isolated in 1977 from *Swertia perennis* L.[30].


(XIV)

A novel xanthone *O*-glycoside, whose *B* ring is partly hydrogenated [compound (XV)] has been isolated from the aerial part of *Gentiana campestris* L.[31].


(XV)

The carbohydrate substituent in xanthone *O*-glycosides usually occupies the 1-position, glycosides with substituents in the 3-, 7- and 8-positions being encountered somewhat more rarely. The first and hitherto only xanthone *O*-glycoside having the carbohydrate substituent in the 5-position was isolated by the present authors from the aerial part of *Swertia iberica* Fish et May[32] and subsequently also from *Swertia connata* Schrenk[33]. The compound called bellidifoloside has the structure of 5-*O*-β-D-glucopyranosyl-1,8-dihydroxy-3-methoxyxanthone (XVI).

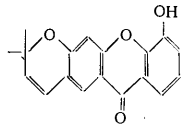

(XVI)

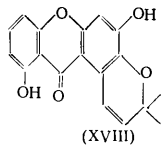
It is of interest to note that, whereas the presence of the carbohydrate substituent in the 2- and 4-positions is characteristic of the xanthone *C*-glucosides, not a single *O*-glycoside with substituents in these positions has been described hitherto. Furthermore, all the xanthone glycosides discovered in nature contain only hydroxy- and methoxyxanthones as aglycones and not a single glycoside has been found whose aglycone contains alkyl substituents and pyran or furan rings.

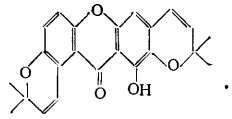
Pyrano- and Furano-Derivatives of Xanthone

Xanthones containing pyran or furan substituents in the molecule have a limited distribution in nature. They have been detected in plants of the families Guttiferae and Polygalacae and also in certain lower fungi.[3,5]

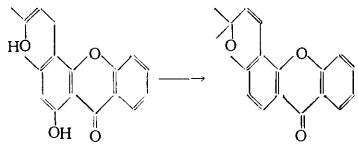
Compounds with one or two pyran rings having the linear and angular structures (XVII)–(XIX) have been described:


(XVII)

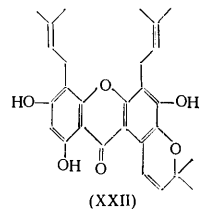

(XVIII)


(XIX)

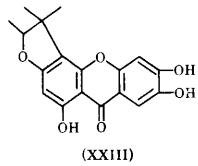
The pyranoxanthones in plants are always accompanied by xanthones with isoprenyl substituents, which are their biogenetic precursors [compounds (XX) and (XXI)]:[34]

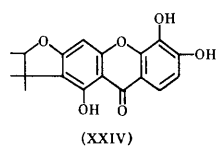

(XX) (XXI)

Partial cyclisation of the isoprenyl chain can lead to the formation of compounds containing simultaneously both the pyran ring and an alkenyl substituent [compound (XII)]:[35]

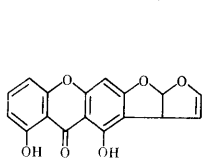

(XXII)

Furanoxanthones have been discovered in nature at the beginning of the 1970's. They have a very limited distribution and have been isolated from certain plants of the family Guttiferae and also from the mycelia of lower fungi. Mainly dihydrofuranoxanthones with a single furan ring [compounds (XXIII) and (XXIV)] are encountered in plants of the family Guttiferae[36,37]:

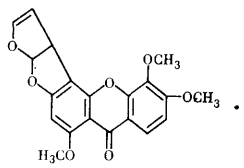

(XXIII)


(XXIV)

The mycelia of lower fungi (certain *Aspergillus* species) contain condensed furanoxanthones [compounds (XXV) and (XXVI)]:[38,39]



(XXV)



(XXVI)

This class of natural xanthones is at present only just beginning to be investigated.

III. CHEMOTAXONOMY OF NATURAL XANTHONES

The distribution and quantitative compositions of natural xanthones have chemotaxonomic importance. A correlation has been found for higher plants between the nature of the substituents in the xanthone ring, their relative positions, and the assignment of the plants to specific families[3,40,41].

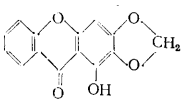
The distribution of xanthones in the family Gentianacae has been studied in greatest detail from this standpoint. Thus the presence of xanthones is characteristic of plants of the genera *Enicostemma, Hoppea, Canscora, Gentiana, Swertia, Halenia, Eustoma, and Frasera.*[42–45].

The importance of polyhydroxyxanthones as a chemotaxonomic marker is mainly limited to the genera *Swertia* and *Gentiana*, where xanthones are encountered most frequently. Thus the distribution of xanthone glycosides has been investigated in very great detail within the limits of individual sub-families of the genus *Gentiana*. Studies have shown that the plants belonging to different sub-families have as a rule a specific set of xanthones and in addition individual plant species within the limits of one sub-family can contain a xanthone glycoside specific only to the given species. For example, the presence of 7,8-dihydroxy-3-methoxy-1-*O*-primeverosylxanthone, 7-hydroxy-3,8-dimethoxy-1-*O*-primeverosylxanthone, and 3,7,8-trimethoxy-1-*O*-primeverosylxanthone is characteristic of the majority of plants in the *Cyclostigma* section. At the same time gentiabavarutinoside (7-*O*-acetylrutinosyl-1,8-dihydroxy-3-methoxyxanthone), discovered in *Gentiana bavarica* L., is absent from the other species of the *Cyclostigma* section investigated. At the same time *Gentiana verna* L. contains 8-*O*-glucosyl-1,7-dihydroxy-3-methoxyxanthone, the only glycoside with the carbohydrate substituent in the 8-position within the limits of the sub-family[3,30,46]. The mode of substitution in the xanthone ring is specific to each sub-family. Thus xanthones with substituents in the 1,3,7,8-positions predominate in the *Cyclostigma* sub-family, whereas 1,3,5,8- and 1,3,4,5,8-substituted xanthones predominate, for example, in plants of the *Amarella* sub-family[47]. The presence of 1-hydroxy-7-methoxy-3-*O*-primeverosylxanthone is characteristic of plants of the sub-family *Coelanthe*[48].

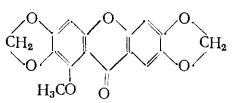
An extremely important chemotaxonomic feature of plants in the family Guttiferae is the presence of pyranoxanthones and xanthones with isoprenyl substituents.

The quantitative compositions of xanthones in plants of the genera *Garcinia*[49], *Calophyllum*, and *Kielmeyera*[50,51] have been studied in greatest detail.

Xanthones containing the methylenedioxy-group are encountered in nature comparatively rarely and their presence in plants is an extremely interesting chemotaxonomic feature. Xanthones with the methylenedioxy-group have been discovered in plants of the families Polygalaceae and Guttiferae. In plants, xanthones with this structure are accompanied as a rule by polyhydroxyxanthones which are partially or completely methylated. In the family Polygalaceae, mono- and bis-methylenedioxy-derivatives of xanthone have been discovered in plants of the genus *Polygala* [compounds (XXVII) and (XXVIII)]:[52–55]

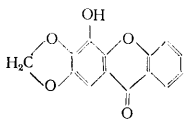


(XXVII)

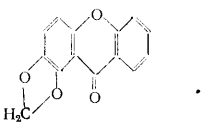


(XXVIII)

In the family Guttiferae xanthones with this structure are encountered in representatives of the genera *Caraipa*[56,57] and Kilelmeyera,[58–61] xanthones with the methylenedioxy-group in the *A* ring predominating in plants of the genus *Kilelmeyera* [compounds (XXIX) and (XXX)]:



(XXIX)



(XXX)

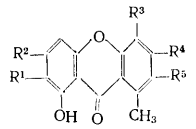
Among all the xanthone glycosides known at the present time, mangiferin is most widely distributed in nature. It has been discovered in plants of almost 20 families[1,v,62,63]. Plants of the families Gentianaceae, Fabaceae, and Iridaceae have the highest content of mangiferin. However, the attempts to establish a regularity in the distribution of mangiferin in plants within the limits of the sub-families of the genus *Gentiana* have not been successful, since mangiferin has been discovered in plants of almost all the sub-families.

Among plants of the family Iridaceae, mangiferin has been sought in various Iris species[64,65]. Although specimens with a very high mangiferin content (1–2.7%) are encountered among the plants of the Iris species investigated, its presence in plants of individual sections shows no particular regularity[64]. The studies on plants of the genus *Hedysarum* (the family Fabaceae) were more successful. Investigations were made of 26 different species belonging to five sub-families of the genus *Hedysarum* (representatives of the sub-family *Spinosissima* were not investigated, since they are virtually not encountered on the territory of the USSR). Mangiferin was detected in 12 plant species belonging to the sub-family *Obscura* and in one plant species belonging to the sub-family *Subacaulia*[62]. Among plants of this sub-family, mangiferin was also detected in *Hedysarum denticulatus* Rgl.[66]. Thus, among plants of the genus *Hedysarum*, a relation is observed between the content of mangiferin and the assignment of the plant to a particular sub-family.

It is also of particular interest to note that, among all the plants of the family Guttiferae investigated at the present time, mangiferin is present mainly in plants of the genus *Hypericum*[63,67]. The systematic study of the mangiferin content in plants of this species is only just beginning.

The structural features of lichen xanthones exhibit a definite regularity: the substituents in the xanthone ring are in the 1-, 3-, 6-, and 8-positions, the 8-position is occupied by the methyl group, the 1-position is occupied by the hydroxy-group, and the 3- and 6-positions are occupied by methoxy-groups [compound (XXXIa)]. In the study of lower plants, lichens were found to possess a novel property consisting in their ability to biosynthesise chloro-xanthones. Chlorine atoms occupy the 2-, 4-, 5-, and 7-positions in the xanthone ring. Di- and tri-chloro-xanthones are encountered most frequently, the tetra- and mono-chloro-derivatives being rarer [compounds (XXXI, b

and c)]:[68-71]



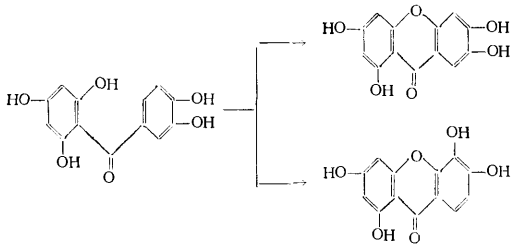
(XXXI)

(a) $R^1=R^3=R^5=H$, $R^2=OCH_3$, $R^4=OH$;
(b) $R^1=R^5=Cl$, $R^3=H$, $R^2=R^4=OCH_3$;
(c) $R^1=R^3=R^5=Cl$, $R^2=OCH_3$, $R^4=OH$.

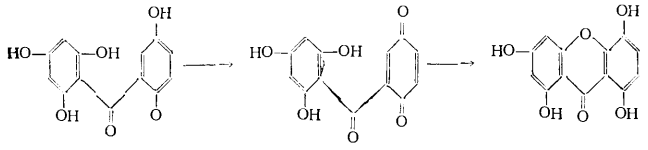
IV. BIOGENESIS OF XANTHONES

At the present time numerous studies on the biogenesis of xanthones have been described in the literature[2,3,72-74]. In higher plants the xanthone compounds with oxygen-containing substituents are biosynthesised by a mixed shikimate–acetate pathway, i.e. intermediates based on shikimic and acetic acid are condensed with formation of polyhydroxybenzophenones, the intramolecular transformations of which lead to the formation of xanthones. The possible mechanisms of such intramolecular transformations are presented in Schemes 1–4.

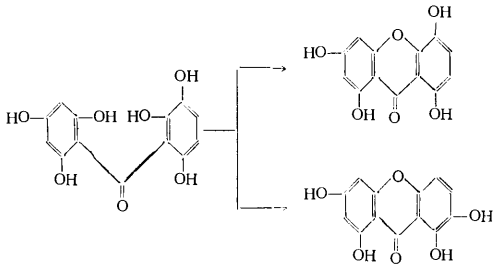
Scheme 1



Scheme 2

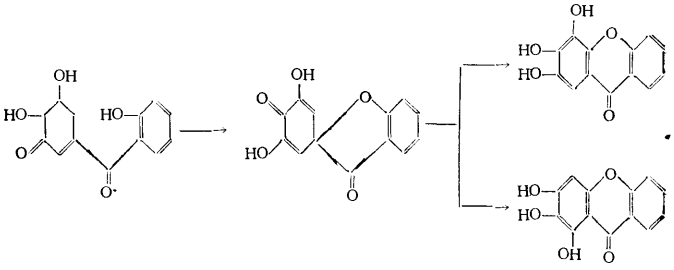


Scheme 3



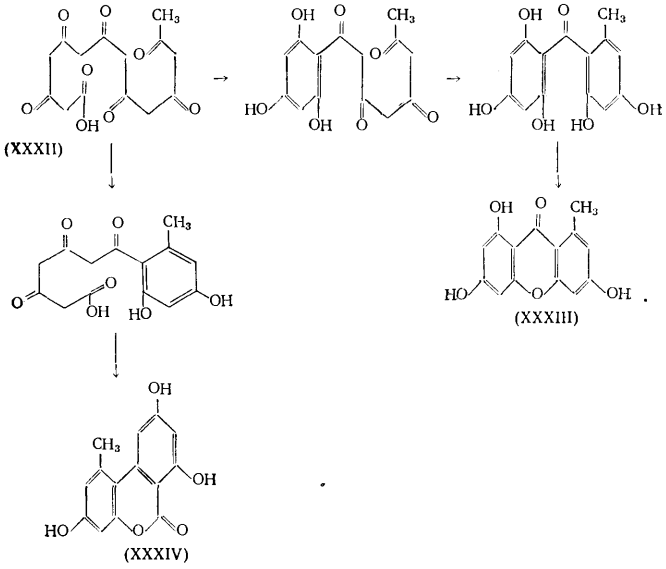
Thus the xanthone structures can be obtained from benzophenones via direct phenolic oxidative addition (Scheme 1), via a quinone stage (Scheme 2), by the dehydration reaction between the OH groups of the ring formed by the acetate mechanism and the ring formed by the shikimate mechanism (Scheme 3), and finally via a spirodiene structure with its subsequent transformation into the xanthone (Scheme 4).

Scheme 4



There exist data showing that direct phenolic oxidation of hydroxybenzophenones predominates in higher plants. The formation of xanthones from compounds having the spirodiene structure is more characteristic of certain micro-organisms, which is confirmed by the joint presence of spirans and xanthones in the latter[50]. In higher plants xanthones have not been isolated together with spirans[2].

The same workers pointed out previously[2] the possible involvement of compounds of the polyketone type in the mechanism of the formation of hydroxybenzophenones. In the study of the biogenesis of lichen xanthones by the chemical synthetic method, the involvement of the poly-β-ketone structure (XXXII) in the formation of norliche-xanthone (XXXIII) was demonstrated[75]:

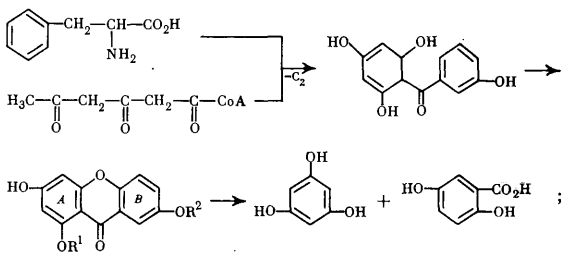


(XXXII) (XXXIII) (XXXIV)

The above scheme shows that there exist two possible reaction pathways for compound (XXXII): as a result of one of these there is a possibility of the formation of the pyranocoumarin (XXXIV), while the other leads to norliche-xanthone (XXXIII). However, in the lichens investigated a pyranocoumarin having the above structure was not detected and the intramolecular transformations of compound (XXXII) in lichens therefore lead to the formation of the xanthone structure.

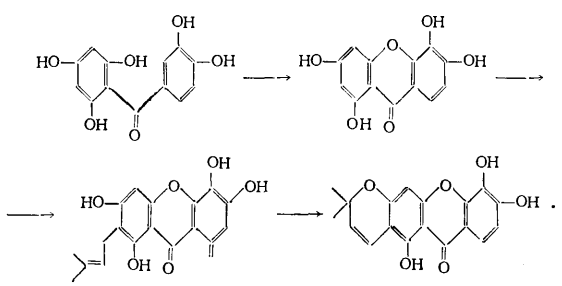
In order to demonstrate the validity of the hypothesis that hydroxybenzophenones are biosynthesised from shikimic acid derivatives and polyhydroxyphenols formed via the acetate pathway, [^{14}C]phenylalanine was injected into *Gentiana lutea* L.[72]. The xanthone derivatives gentisin (XXXV) and isogentisin (XXXVI), containing, as shown by

the analysis of the pyrolysis products, the radioactive label in the *B* ring, were then isolated from the plant:



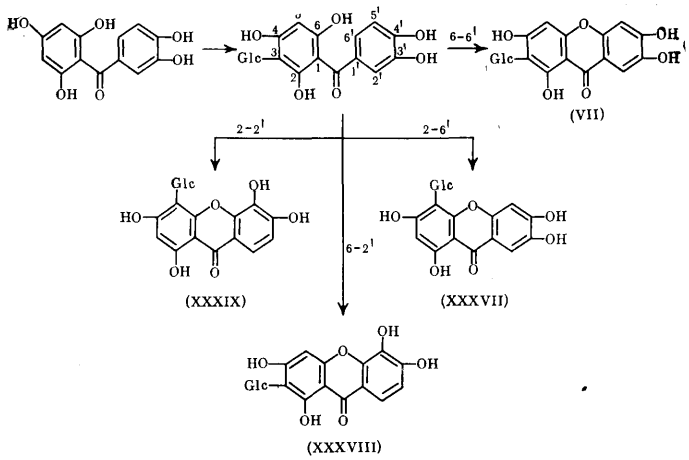
CoA = coenzyme A, $R^1 = CH_3$, $R^2 = H$; $R^1 = H$, $R^2 = CH_3$.

In the study of the biogenesis of pyranoxanthones and xanthones containing isoprenyl derivatives, it was established that the isoprenyl substituent is introduced in the *ortho*- or *para*-position relative to the OH group after the formation of the xanthone structure, this being followed by the closure of the isoprenyl chain at the neighbouring hydroxy-group, which leads to the formation of a pyran ring:



The validity of the assumptions made is confirmed by the simultaneous presence in plants of benzophenone precursors and the corresponding "daughter" xanthones with isoprenyl substituents and pyran rings[34,51,76].

The possible pathways in the biosynthesis of xanthone glycosides have been investigated by introducing labelled precursors of the intermediate benzophenones into *Anemarrhena asphodeloides* Bunge[73]. It was found that glycosylation precedes the formation of the xanthone structure; there is then a possibility of four versions of the closure of the γ-pyrone ring (see below). The proposed mechanism has been confirmed by the isolation of mangeriferin and isomangeriferin (XXXVII) from *Anemarrhena asphodeloides* Bunge[17] and of 2-*C*-β-D-glucopyranosyl-1,3,5,6-tetrahydroxyxanthone (XXXVIII);[20] only 4-*C*-glucosyl-1,3-5,6-tetrahydroxyxanthone (XXXIX) has not so far been detected in nature.



(VII)

(XXXIX) (XXXVII)

(XXXVIII)

V. METHODS FOR THE DETERMINATION OF THE STRUCTURES OF XANTHONES

For the isolation of xanthones, the plant starting material is ground and extracted by the usual methods using, as a rule, solvents with increasing polarity: petroleum ether, chloroform, and methanol[77-79], hexane and acetone[80], ether, acetone, and ethanol[81], etc. Xanthones are extracted usually from lichens using acetone as the solvent, this being followed by treatment of the evaporated extracts with alkali[82-84].

When the starting material is treated with non-polar solvents, mainly the aglycones are extracted. Glycosides are usually extracted with polar solvents after the separation of the total aglycones. The compounds are purified by recrystallisation and also by column and thin-layer chromatography[3]. Apart from thin-layer and column chromatography, gas–liquid chromatography of the TMS-derivatives of xanthones[89] as well as high-pressure liquid chromatography[90,91] have been used successfully for the qualitative and quantitative analysis. The separation by liquid chromatography has been investigated in relation to the compounds obtained from plants of the genus *Gentiana*. A satisfactory separation of the positional isomers has been achieved.

The structures of xanthones are nowadays determined using extensively physicochemical methods such as ultraviolet and infrared spectroscopy, ^1H NMR, mass spectrometry, and X-ray diffraction analysis[39,92].

1. Ultraviolet Spectroscopy

This method is used mainly to determine the positions of the OH groups in the xanthone nucleus. It has been established that the ultraviolet spectra of all natural xanthones are characterised by four intense bands regardless of structural differences: $\lambda_{max}(E)$ = 230–260 nm (20000 – 50000), 260–350 nm (6000 – 28000), 285–300 nm (3000 – 10000), and 325–395 nm (3000 – 12000) [4] (Fig.1).

Sometimes the number of bands increases to five or diminishes to three, but the characteristic spectrum with a specific ratio of the intensities of the short-wavelength and long-wavelength maxima is in general retained. Thus, a given substance can be assigned to the class of xanthones

on the basis of the nature of the absorption in the ultraviolet. In order to determine the location of the OH groups, ionising and complex-forming additives are employed. The ionising additives are usually sodium acetate, methoxide, or ethoxide or caustic alkalis. Thus, in the presence of a free OH group in the 3- or 6-position, the ultraviolet spectrum of the compound in the presence of sodium acetate exhibits a bathochromic shift of the long-wavelength maximum in the range 300–330 nm.

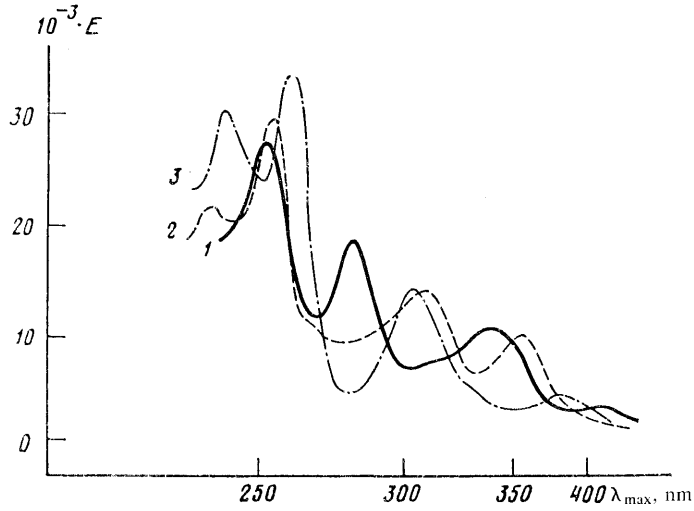


Figure 1. Ultraviolet spectra of xanthones with different modes of substitution in the nucleus (solvent–methanol): *1*) 1,5,8-trihydroxy-3-methoxyxanthone; *2*) 1,3,6,7-tetrahydroxyxanthone; *3*) 1-hydroxy-3,7,8-trimethoxyxanthone.

The OH groups in the 1- and 8-positions can be detected and the presence of the *ortho*-dioxy-group in the molecule can be demonstrated with the aid of complex-forming additives. $AlCl_3$ and boric acid in the presence of sodium acetate are most widely employed for such purposes. The presence of OH groups in the 1- and 8-positions is indicated by the bathochromic shift of the short-wavelength maximum in the range 260–335 nm by approximately 20 nm in the presence of $AlCl_3$. Despite the fact that in the presence of $AlCl_3$ the bathochromic shift of the long-wavelength maximum is about 60 nm, the more intense short-wavelength maximum is used in the test for the presence of the OH groups in the 1- and 8-positions[93,94]. The *ortho*-dioxy-groups also form a compound with $AlCl_3$, but such a complex decomposes in the presence of hydrochloric acid. Boric acid in the presence of sodium acetate, which causes a bathochromic shift of the long-wavelength maximum, is used in the test for the *ortho*-dioxy-groups.

The addition of sodium methoxide to an analytical solution of xanthones can be used to detect vicinal OH groups. This constitutes the optical version of the Bargellini reaction and is manifested by the absence from the ultraviolet spectrum of the four absorption maxima characteristic of the xanthone structure[95,96] (Fig. 2).

2. ^{1}H NMR

^{1}H NMR is a method which yields most information for the determination of the structures of xanthones as regards the nature and relative positions of the substituents. There have been a number of studies in which the proton spectra of hydroxy- and methoxy-xanthones, recorded in different solvents, were analysed[97–99].

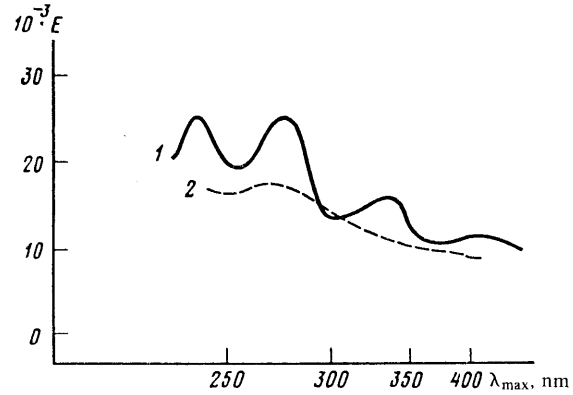


Figure 2. Changes in the ultraviolet spectrum of swertiaperennin (1,2,3-trihydroxy-7,8-dimethoxyxanthone) in the presence of $NaOCH_3$ (solvent–methanol): *1*) swertiaperennin; *2*) ditto plus $NaOCH_3$.

The aromatic protons of xanthones are manifested in the range 6.00–8.05 p.p.m. If the compound is a glycoside, then also the aliphatic protons of the carbohydrate substituents are observed in the range 3.00–5.60 p.p.m.[79] The protons of the aromatic methoxy-groups give rise to signals in the range 3.80–4.10 p.p.m. The ^{1}H NMR spectrum of a hydroxyxanthone recorded in dimethyl sulphoxide exhibits in the range 12–14 p.p.m. the signal of the protons of the OH groups in the 1- and 8-positions, while the proton signals of the OH groups in the other positions of the xanthone nucleus are displaced upfield to 9–11 p.p.m. The ^{1}H NMR of acetylxanthones has been used successfully recently for the determination of the structures of xanthones[79,100]. Thus signals in the range 2.40–2.50 p.p.m. (solvent–chloroform) indicate the presence of the acetyl substituent in the 1- and 8-positions, while the acetyl substituents in the other positions of the aromatic nucleus are manifested in the range 2.30–2.35 p.p.m. The signals of the protons of the aliphatic acetyl groups are displaced to a still stronger field—1.90–2.20 p.p.m. (Fig. 3).

The protons of the aromatic ring containing the chelate hydroxyl (OH groups in the 1- or 8-position) give rise to signals in a stronger field than the corresponding protons of the ring without a chelate hydroxyl. This can be accounted for by the higher electron density in the ring owing to chelation. In the case of glycosides this effect is observed most effectively in solution in deuteriated DMSO.[4]

The signals of the protons of the methyl groups of the isopropenyl substituent in the xanthone molecules are usually manifested as three-proton singlets in the range 1.1 to

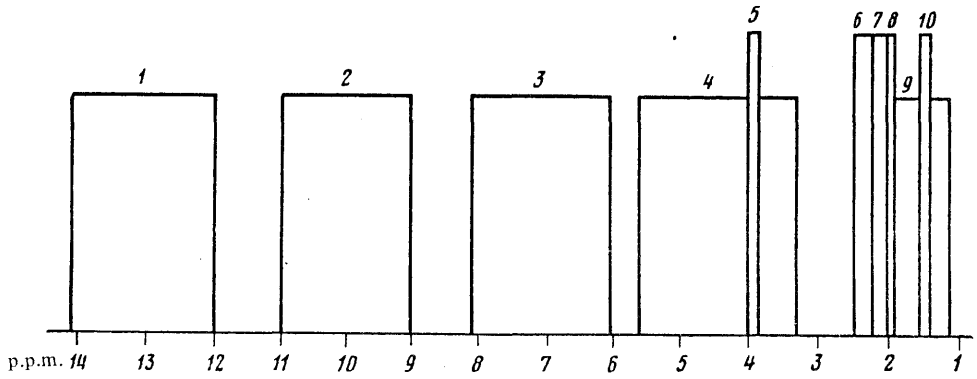


Figure 3. The proton chemical shifts in the ^{1}H NMR spectra of xanthone derivatives: *1*) OH groups in the 1- and 8-positions; *2*) OH groups in the 2–7-positions; *3*) aromatic protons; *4*) aliphatic protons; *5*) protons of aromatic CH_3O groups; *6*) protons of the CH_3OCO group in the 1- and 8-positions; *7*) protons of the CH_3OCO group in the 2–7-positions; *8*) protons of the carbohydrate component; *9*) protons of the $(CH_3)_2C=$ group; *10*) protons of the $(CH_3)_2C$ group.

1.8 p.p.m.[5]. The signals of the protons in the angular methyl groups in the molecule of a pyranoxanthone are observed in the range 1.4–1.5 p.p.m. (Fig.4).

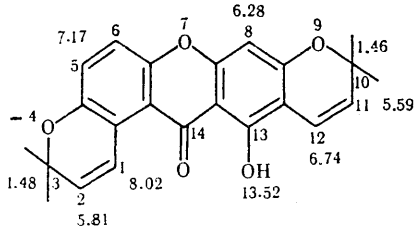


Figure 4. Distribution of the proton chemical shifts (p.p.m.) in pyranoxanthone[101].

Fig.4 shows that the chemical shifts of the protons in the 2- and 11-positions of the pyran ring are displaced upfield relative to the signals of the protons in the 1- and 12-positions, which can be accounted for by the electron-donating influence of the protons of the angular methyl groups at the C(3) and C(10) atoms.

The problem of the site where the carbohydrate component is attached frequently arises in the determination of the structures of xanthone glycosides. The exhaustive methylation method with subsequent hydrolysis of the glycosides proved to be extremely effective for the solution of this problem. Furthermore, direct comparison of the spectra of the glycosides and their aglycones yields information about the site of addition of the carbohydrate component to the xanthone nucleus. The spin–spin interaction constant for the signal of the anomeric protons of the glycosidic centre yields information about the nature of the glycosidic linkage.

The Overhauser effect has also been used to elucidate the positions of the substituents in the xanthone nucleus[102].

^{13}C NMR has been used successfully in recent years for the determination of the structures of xanthones[103–105]. The ^{13}C NMR spectra of polyhydroxyxanthones (aglycones, *O*- and *C*-glycosides) have been investigated. ^{13}C NMR spectroscopy is of special diagnostic importance for the determination of the nature of the relative positions of the monosaccharides in diglycosidic substituents[4].

3. Infrared Spectroscopy

The assignments in the infrared spectra of xanthones are complicated by the strong interaction of the vibration of the carbonyl group and the C=C bonds of the γ-pyrone ring. According to some data[106], the highest-frequency 1660 to 1670 cm^{-1} band in the range 1500–1700 cm^{-1} has been assigned to the vibrations of the carbonyl group. However, further investigations showed that this band is due to the vibrations of the C=C bonds of the γ-pyrone ring, while the vibrations of the C=O group give rise to a band in the range 1620–1640 cm^{-1}.[4,107]

Santesson[108] investigated the infrared spectra of lichen polyhydroxyxanthones in the range 1500–1700 cm^{-1}.[108] It was found that the frequency of the band corresponding to the C=O group is reduced by 15–25 cm^{-1} after the introduction of an OH group in the 1-position. This effect is evidently due to chelation, since alkylation or esterification of the OH group returns the frequency of the C=O group to its previous value.

Klimenko et al.[109] carried out a theoretical calculation of the vibrations of the xanthone molecule; the symmetry of certain vibrations was determined from the dichroism of the infrared bands.

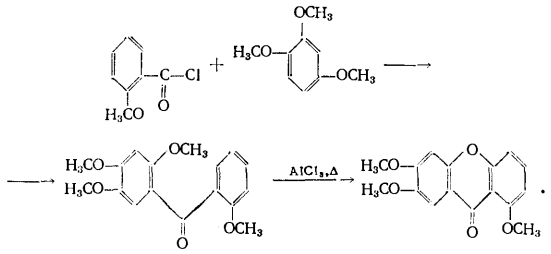
The band in the range 3200–3500 cm^{-1} in the infrared spectra of hydroxyxanthones is due to the vibrations of the chelate hydroxyls, while the bands in the range 1500 to 1600 cm^{-1} are assigned to the vibrations of the aromatic C=C bonds. The region below 1500 cm^{-1} is specific to each compound and can be used successfully for the identification of xanthones.

Mass spectrometry has been used widely in recent years for the determination of the structures of xanthones. Aritomi et al.[110] used this method in the study of the fully acetylated derivatives of mangiferin and isomangiferin. The mass spectra of xanthone *O*-glycosides do not contain the characteristic molecular peak, but the molecular peak of the aglycone (M^+) and the nature of its fragmentation yield information about the structure of the substance. Thus the mass spectra of hydroxyxanthones usually exhibit signals due to the fragments (M^+-OH), (M^+-CO), and (M^+-CHO). When one or several methoxy-groups are introduced into the xanthone, its mass spectrum shows signals due to the fragments (M^+-CH_3), (M^+-CH_2O), and (M^+-CH_3CO).[111,112] The presence of a weak molecular peak has been noted in the fully methylated derivatives of xanthone *O*-glycosides[4].

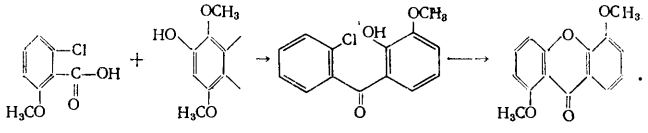
VI. SYNTHETIC CHEMICAL METHODS IN THE STUDY OF NATURAL XANTHONES

The preparation of synthetic xanthone derivatives was used previously only to confirm the structures of natural xanthones[1]. At the present time the applications of synthesis in the study of natural xanthones have expanded and make it possible to solve certain biogenetic problems. Furthermore, chemical synthesis is used to prepare biologically active natural xanthones.

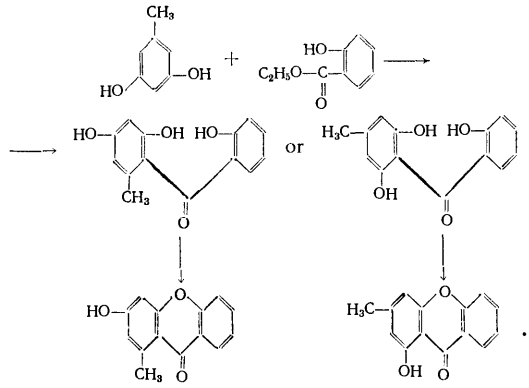
One of the common reactions used to synthesise xanthones is the Friedel–Crafts reaction between aromatic carboxylic acid chlorides and polyhydroxyphenols[113–116]. The corresponding benzophenone is an intermediate. The benzophenone cyclises to the xanthone on heating the reaction mixture to 200–220 °C.[117] If polymethoxyphenols are involved in the reaction, then the benzophenone formed as an intermediate undergoes partial demethylation in the *o*-position relative to the carbonyl group. Aluminium chloride is usually employed as the dimethylating agent[113,118]:



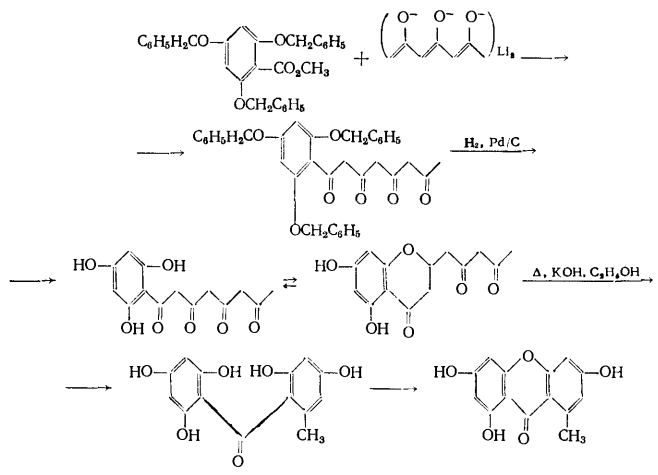
If *o*-chlorobenzoic acids are used in the reaction, then the cyclisation of benzophenone to the xanthone takes place under milder conditions[117]:



Xanthones can be obtained by the cyclocondensation of phenols with methyl or ethyl *o*-hydroxyarenecarboxylates in diphenyl ether[119]:



In the modelling of processes occurring in the biogenesis of xanthones in lichens, an aldol-type cyclisation of 1-(2,4,6-trihydroxyphenyl)octane-1,3,5,7-tetraone was used to prepare natural xanthones. The corresponding benzophenone is formed as an intermediate, undergoing subsequent dehydration[75]:



(XXIX)

The acid-catalysed cyclocondensation of hydroxy-derivatives of diphenyl ether and phosgene[120] and also the intramolecular cyclisation of 2-carboxy-derivatives of diphenyl ether[121] can be used to synthesise polyhydroxy-xanthones.

A reaction involving the synthesis of xanthones from ω-acetoxy-2-acylcyclohexanones has been described[122].

The most convenient method of synthesising pyrano-xanthones has been developed by Locksley and coworkers[123–126]. It is based on the synthesis of 2-alkyl-1-hydroxyxanthones from 1-allyloxyxanthones by the Claisen rearrangement with subsequent modification of its side chain. The derivatives of 1-hydroxy(3-methylbut-2-enyl)xanthones obtained in this way are treated with hydrobromic or hydriodic acid. Depending on the reaction conditions, angular or linear pyranoxanthones are obtained.

The syntheses of xanthone glycosides have been investigated. The addition of the glycosidic residue to the aglycone takes place via a reaction involving the condensation of the aglycone with acetyl-α-D-glycosyl bromide, the formation of both *C*- and *O*-glycosides being possible depending on the reaction conditions. Thus, when the

reaction is carried out in methanol in the presence of sodium methoxide, the hydrocarbon substituent adds to the aglycone via a C–C bond[118]. *O*-Glycosides are formed when the reaction is carried out in pyridine in the presence of silver carbonate[127,128].

VII. PHARMACOLOGY OF XANTHONES

Plants containing xanthones have been used for a long time in Soviet medicine[129,130]. Current research has shown that xanthones exhibit an extremely wide variety of pharmacological activities. Antidepressant, antimicrobial, cardiotonic, diuretic, and antiviral activities of xanthones have been noted.

The stimulating activity on the central nervous system (CNS) and the antitubercular activity of certain natural and synthetic derivatives of xanthones have been investigated in greatest detail.

The search for natural compounds with antidepressant activity has been prosecuted mainly among plants of the family Gentianaceae[131]. Xanthones differing in the number and relative positions of hydroxy- and methoxy-groups have been the object of study. It was noted that the aglycones[130] and also the xanthone *C*-glycoside mangiferin[132] have the most marked antidepressant activity. The fact that the xanthone *O*-glycosides have in fact a depressant activity on the CNS and an anticonvulsant activity proved to be of very great interest[133]. However, natural xanthones do not exhibit a clear-cut relation between the nature of the antidepressant activity and structure. In order to investigate in greater detail the dependence of the nature and strength of the antidepressant effect on the structure, a series of semisynthetic methoxy-amino- and chloro-xanthones substituted in the 2-, 3-, 4-, and 6-positions were screened[134,135]. The introduction of the hydroxy-group in the 3-position increased the activity of the xanthone compound and substitution of the 6-position by a chlorine atom greatly altered the nature of the antidepressant activity and increased the toxicity of the compound.

The studies on the antitubercular activity of natural xanthones proved to be extremely fruitful[136,137]. Thus, in the investigation of xanthones from the ethanol extract of *Canscora decussata* Achult, it was observed that the sum of the aglycones has a more marked tuberculostatic activity than the xanthones and the glycoside mangiferin[138]. In order to investigate in greater detail this behaviour, a study was made of fourteen natural and semisynthetic xanthones differing in the positions of the hydroxy- and methoxy-groups and in the presence or absence of a carbohydrate substituent[139]. Experimental results revealed a definite relation between the type of substitution in the xanthone nucleus and the tuberculostatic activity: the activity of xanthones is manifested in the presence of hydroxy- or methoxy-groups in the 1,3,5,6- or 1,3,8-positions in the xanthone nucleus. With increase of the number of hydroxy-groups in the above positions, the activity rises. Thus 1,3,5,6,7- and 1,3,6,7,8-pentahydroxyxanthones proved to be the most active. When a carbohydrate substituent is introduced into the molecule, the activity falls.

3,6,8-Trihydroxy-1-methylxanthone, with appreciable antibacterial activity, has been isolated from the metabolic products of *Penicillium patulum*.[140]

Studies on the antitumour activity of natural xanthones have been started in recent years. Thus 1,6-dihydroxy-xanthones and 1,3-dihydroxyxanthones among the 18 natural xanthones isolated from *Mammeae americana* were found to have an appreciable inhibiting activity in relation to sarcoma 180.[141]

1,8-Dihydroxy-3-methylxanthone, which exhibits an antifungal activity, was obtained from the defatted seeds of *Cassia tora*. The compound manifested an activity in relation to certain *Trichophyton*, *Microsporum*, and *Geatrichum* species in the presence of 100 mg ml^{-1} of L-ascorbic acid as the antioxidant[10]. An antifungal activity in relation to certain *Fusarium* species has also been noted in mangiferin[142,143].

Mangiferin is the most thoroughly investigated xanthone derivative from both physicochemical and pharmacological points of view. Apart from its stimulating effect on the CNS,[132] it exhibits cardiotonic and diuretic effects[144], influences the water metabolism[145], and has some antitubercular activity[138,142,143]. Medicinal forms of this substance have been developed: tablets, suppositories, and solutions for injection[144].

The results of a pharmacological study of mangostin [3,6,8-trihydroxy-2-methoxy-1,7-di(3-methylbut-2-enyl)-xanthone] and its derivatives were published in 1979.[146] Almost all the compounds have a depressant effect on the CNS and in addition the 3,6-di-*O*-glucoside of mangostin has a stimulating effect on heart muscle and increases blood pressure. Mangostin, 1-isomangostin, and mangostin triacetate have an appreciable anti-inflammatory activity, manifested even in the case of bilateral adrenalectomy in rats; mangostin has also been found to have an antiulcer activity.

Together with the study of natural xanthones, investigations have been made in recent years of the pharmacological properties of synthetic xanthone derivatives in order to carry out specific syntheses of compounds with a specified spectrum of pharmacological activity.

The synthesis of various alkylaminoxanthones constitutes the most interesting trend. Thus Fleming and coworkers[147] synthesised a series of di(aminoacetyl)xanthones which act against certain viruses affecting warm-blooded animals, including the viruses of encephalomyocarditis, the viruses of the herpes group, etc.

Baum[148] investigated the antiarrhythmic activity of bis(dialkylamino)ethoxyxanthones in experiments on dogs. The highest activity was noted in 1,6-bis-2-di-(isopropenylamino)ethoxyxanthone.

Studies on the pharmacological activity of various derivatives of xanthone-2-carboxylic acid, which proved to be active in asthmatic conditions, have been of very great interest[149]

* * *

The studies carried out hitherto on natural xanthones undoubtedly demonstrate their enormous value as regards the creation of new medicinal preparations. The continually growing interest in this type of compound is indicated by the fact that in recent years studies have begun on the mechanism of the pharmacological activity of xanthones at the biochemical level. Thus, in connection with the investigation of the stimulating effect of natural xanthones on the CNS, detailed studies have been made of the mechanism of the inhibition of monoamino-oxidase by isogentisin and its 3-*O*-glucoside.[150] The relation between the structures of xanthones and their ability to inhibit AMP phosphodiesterase has been investigated[151].

There is no doubt that further more profound studies on these lines will extend the pharmacological applications of natural xanthones.

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In the Vanguard of Chemical Progress (Jubilee of *Uspekhi Khimii*)

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In 1982 fifty years have elapsed since appearance of the first issue of the periodical *Uspekhi Khimii*.

This journal was founded at the beginning of the 1930s by a decision of the USSR State Education Committee to publish the most important reviews in the field of theoretical and experimental chemistry and chemical technology, as indicated in the first editorial statement[1]. This had serious methodological or generalising value and resulted from constructive critical thought combining the most recent scientific advances into a single elegant whole. It has now become the leading publication of the USSR Academy of Sciences having comprehensive chemical interest, on whose pages are fully reflected all aspects of the development of chemical science in our country and abroad.

For a long period of time now, coinciding with exceptionally vigorous development of chemical science, *Uspekhi Khimii* has performed successfully two important and worthy functions. Firstly, the journal is the most authoritative vehicle for the most recent theoretical and practical achievements of Soviet chemists, regularly acquainting the international chemical community with them. The reviews carry great weight and authority, since they have usually been presented as serious scientific and analytical summaries of the results of many years' experimental or theoretical investigations by whole teams of scientists, which had already been approved either as ordinary papers or at congresses and conferences, and in several cases have been incorporated into current practice. The second function of the journal is to acquaint the Soviet specialist reader with the most important achievements of world chemistry and cognate disciplines, with the best reviews, and with current trends. Since chemical science in our country, while retaining, of course, all its national, organisational, and historic features and traditions, also constitutes an extremely authoritative part of the world chemical community, making its own original contribution to the general development of this science, these two scientific information functions have long been the principal characteristics of the activity of the journal: *Uspekhi Khimii* is now one of the most authoritative vehicles of the international policy of world scientific collaboration, contributing by its work to the comprehensive development of current scientific and technical progress.

Analysing the various aspects of the many sided scientific informational, educational, and also organisational activity of the journal, reflecting the growth in its international authority, it is of interest to recall the creative history of *Uspekhi Khimii*, in order to assess through the prism of its most important scientific papers the contribution that academic chemists have made to the development of Soviet chemical science and industry, to the establishment and elaboration of new branches and trends, also to the organisation and growth of the chemical press and chemical education, and to the training of scientific and technical personnel in our country.

Five main periods of activity of the journal can now be distinguished—an initial stage (from the founding to the beginning of the 1940s), its work during the years of the Great Patriotic War (1941–1945), then the first postwar decade, the 1950s and 1960s, and the present stage—each period characterised by definite scientific and organisational experience, reflecting the efforts by members of its

editorial boards and all its authors and collaborators, which has now served the scientific training of several generations of research chemists.

The initial stage, associated with the names of the founders of the journal (N.P.Gorbunov, A.N.Bakh, A.M. and B.M.Berkengeim, E.V.Britske, S.I.Vol'fkovich, V.V.Potemkin, N.D.Zelinskii, N.S.Kurnakov, and A.N.Frumkin), was distinguished by exceptional fruitfulness. In view of the long absence of a chemical review journal of our own together with a large accumulated scientific potential, due both to many years of work by older generations of chemists and to the influx of fresh scientific and technical personnel, the main value of the journal during those years lay chiefly in its informational and organisational functions both in fundamental science and in the practical application of chemical advances to the national economy.

Founded in the circumstances of the industrial upsurge of the early five-year plans, *Uspekhi Khimii* responded promptly during those years to the most urgent problems of the chemical industry then being established in the USSR. The first issue already containing the full text of the directive by the USSR State Planning Committee and the Committee on Chemicalisation of the National Economy to draw up a plan for scientific research on chemistry and chemical technology[2], in which growth of the chemical industry depended on solving problems of fuel and power (the efficient industrial utilisation of petroleum, coal, lignite, bituminous shales, and peat, and also the liquefaction of solid fuel), working out the most effective technical chemical processes in ferrous, non-ferrous, and electrical metallurgy (development of flotation methods, formulation of novel metal alloys, in particular acid-resistant, heat-resistant, and high-speed steels, protection of metals from corrosion, use of oxygen in metallurgical processes, extraction of light metals—lithium, sodium, beryllium, magnesium, aluminium), chemicalising agriculture and forestry (the search for combined and concentrated organic and inorganic fertilisers, use of new insecticides, development of agricultural chemistry and biochemistry), and finally developing further mineral and organic technology with the aim of obtaining inorganic and organic substances, products, and materials†.

The pages of the journal reflect during those years the problems of combining power–chemical, metallurgical–chemical, and purely chemical processes in single industrial units, aspects of the study of rare and radioactive elements with procedures for their isolation and separation, technological features of the production of ammonia, chlorine, bromine, and iodine, improvements to the cracking of petroleum, the manufacture of synthetic rubber, dyes, artificial fibres, and plastics, medicinals, surface-active agents and perfumes, lubricating oils, and many other products of industrial importance.

The journal paid close attention also to raw-materials problems. The first issue already contained a paper# by A.E.Fersman on "New Problems in the Study of Mineral Resources", devoted to aspects of the utilisation of air, clay, sand, quartzites, and nephelines in large-scale combined production. Together with problems of the technology of natural resources (metals, sodium carbonate, cement, silicates) several papers examined aspects of the widespread industrial use also of agricultural resources (manufacture of alcohol, acetone, acetaldehyde, furaldehyde, acetic acid), the development of biochemical methods for increasing the content of valuable substances in plants (fibres, oils, fats, ethers, esters, starch, glycerol, proteins, vitamins, alkaloids, and tanning agents), and also the production of important organic compounds (hydrocarbons, ethylene, acetylene, butadiene, fatty acids). Effective use of solar energy was regarded as having promise for the future.

Papers in the journal during those years responded also to problems involved in establishing and developing new provincial industrial complexes. Thus aspects of the investigation of natural salt equilibria in terms of physicochemical analysis, developed in N.S.Kurnakov's school, were examined in the paper "The Kara-Bogaz-Gol Problem"; a special paper was also concerned with prospects for industrial organic synthesis associated with construction of the Kuibyshev hydroelectric station and the Second Baku.

Industrial growth in chemical fields of the national economy should be based on an intensification of fundamental scientific research, directed primarily at study of the structure of matter by the latest physical methods, development of the theory of catalysis and chemical kinetics, study of surface phenomena (including adsorption), application of new physicochemical methods to solve problems of organic chemistry, development of new production processes based on novel catalytic reactions, application of the methods of colloid chemistry, and study of solid-phase and photochemical reactions, as well as the chemistry of ultrapure substances.

Among the chief administrative measures taken to secure such investigations were development of a network of general and specialised research institutes and up-to-date works laboratories, and also expansion of the research activity of higher educational institutions with intensified training of personnel for scientific research (in 1939 the journal published the slogan of the Mendeleev All-Union Chemical Society "Youth for Science!").

Thus the historical circumstances of these years themselves promoted in every possible way conversion of the first native academic review journal into a unique and most authoritative forum of science, information and organisation to bring together the combined efforts of all investigators developing new lines of chemical research in the country.

Analysis of the activity of the journal shows that it coped with the task entrusted to it, many of its papers on fundamental science paving the way for current chemical trends. From a methodological point of view, perhaps the most considerable achievement of *Uspekhi Khimii* during the initial period was to develop its own original scientific personality, with an independence and systematic strategy for interpreting current chemical advances. The strategy consisted in particular in orienting the journal towards quantitative features of various aspects of chemistry and elucidating the physical nature of the principles underlying chemical changes.

Although the journal has on the whole preserved its chemical character from its founding till the present time, its editorial board realised even during the initial stage that future progress in all chemical sciences would be determined in considerable measure by advances in contemporary theoretical and experimental physics, including quantum mechanics. In the opinion of I.Langmuir, a paper by whom was published in the journal§, theoretical scientific research is of

†One detail indicating the active organising work of the editorial board of *Uspekhi Khimii* was a special note asking readers to send in their additions to this plan, for consideration by the Chemicalisation Committee in the subsequent planning of scientific research topics.

#Precise references to all the papers discussed subsequently in the survey can be found from keywords in review titles or from the reviewers' names in the appropriate subject and author indexes[3].

§The work of foreign investigators was published in *Uspekhi Khimii* during those years either as Russian translations of contributions to international periodicals or as specially commissioned papers and reviews by leading specialists.

immense value to mankind. However, although theoretical physics underwent an exceptional flowering precisely during those years, the validity of a so-to-say "physical" orientation for a chemical publication was nevertheless far from obvious at that time, and it is only now that, while giving credit to the scientific intuition of the journal, we are able to assess the correctness of the path chosen.

Among purely physical contributions of those years ("Physics of the Nucleus" by P.Debye, "Atomic Structure and Chemistry" by B.F.Ormont, "New Elementary Particles" by E.V.Shpol'skii and later D.D.Ivanenko, "Nuclear Reactions" by S.Z.Roginskii, and "Isomeric States of Atomic Nuclei" by A.A.Grinberg) work on natural and artificial radioactivity and the production of new elements (protactinium, neptunium, technetium, francium) attracted especial attention from the journal. As always, preference was given to original sources, i.e. contributions by the most authoritative workers in these fields (F.Joliot and I.Joliot-Curie's "On the Artificial Production of Radioactive Elements", O.Hahn's "Application of Radioactive Methods to Chemistry" and "Chemical Elements and Natural Forms of Atoms", L.Meitner's "On Artificial Radioactivity" and I. and W.Noddacks' "Current State of Theories of Radioactive Disintegration").

The reader was kept regularly informed of advances in research on nuclear fission (papers by F.Joliot and N.Bohr on "New Work on the Splitting of Uranium and Thorium Nuclei" and "Spontaneous Fission of Uranium"), and briefly acquainted annually with the current literature on nuclear physics, with sessions of the Physics Group of the USSR Academy of Sciences, and also with foreign and All-Union scientific conferences (we may note I.V.Kurchatov's report on the 1940 All-Union Meeting on the Physics of the Atomic Nucleus). As a consequence of such effective operations by the journal every chemistry specialist who regularly examined its contents could be kept informed on the most recent scientific advances in these fields during all those years.

The achievements of nuclear physics and the discovery of new elements aroused great interest at the time in the structure of Mendeleev's Periodic System of the Elements and in the nature of the Periodic Law. The journal satisfied readers' interest in these problems extremely fully, with articles by such authorities as E.Rutherford ("The Periodic Law and its Interpretation"), L.Meitner ("Atomic Weight in Present-day Science"), and V.G.Khlopin ("Transmutation of Elements and the Periodic Law"); that by B.M.Kedrov refined the very concept of "chemical element".

Progress in all these scientific fields would have been inconceivable without the creation of a universal theoretical apparatus to describe microphenomena—quantum mechanics—the current state of which was presented in E.Schrödinger's paper. Among its contents, the journal revealed also the contemporary quantum-chemical treatments of such concepts as "chemical bond" and "valency", by linking analytical papers on this important topic with instructive surveys in the 1940 Section "Aid to the Chemistry Instructor in Higher Education", in which Ya.K.Syrkin, M.E.Dyatkina, and A.A.Zhukhovitskii were active.

Another important feature of the quantum mechanics of those years reflected in the papers of *Uspekhi Khimii*, besides its contribution to pure physics and the study of molecular structure, was its incipient penetration even into chemistry. The development of quantum mechanics at that time acted as a powerful stimulus to that of several classical fields of physical chemistry (e.g. the quantum-mechanical adsorption theory of D.Blokhintsev and S.Shekhter), and to the establishment of a basis for a new and independent branch of science—chemical physics, whose object was to investigate the fundamental physical principles of chemical reactions.

Since many of the fundamental successes of chemical physics in understanding the physical essence of chemical processes occurred precisely in prewar decades, it is remarkable that establishment of the journal *Uspekhi Khimii* (1932) almost coincided in time with foundation of the USSR Academy of Sciences' Institute of Chemical Physics (1931), the first in the world, whose chief scientific interests and achievements (a physical basis for the concepts of valency and chemical affinity, investigation of chemical kinetics and construction of a theory of primary chemical processes in gas and condensed phases, study of the mechanism of energy exchange and transfer in chemical reactions, development of new physical research methods), and also the production of novel substances and materials (e.g. artificial diamonds—O.I.Leipunskii) are reflected in the pages of the journal from the very early years right until the present time.

N.N.Semenov's paper "Chemical Forces and the Theoretical Foundations of Chemical Kinetics" in the first issue already drew attention to the inability of classical physical chemistry—based on thermodynamics, which is concerned with equilibrium states (and therefore, in the author's opinion, would have been more correctly termed *thermostatics*)—to provide a true understanding of the dynamic process of chemical change, i.e. to solve the main problem of chemical physics, which is to calculate absolute rates and activation energies of chemical reactions. This paper suggested that the theoretical principles of chemical kinetics should be based on atomic structural data treated by quantum mechanics; methods for estimating forces of chemical affinity from the analysis of continuous and line spectra and use of these results in chemical dynamics were given for several thermal and photochemical reactions, including various types of dissociation and association stages and energy-exchange processes.

Prewar decades, which coincided with the years during which the scientific activity of the journal was initiated and developed, were characterised by exceptional progress in chemical physics, especially in those branches concerned with formulating a theory of primary chemical processes. *Uspekhi Khimii* showed great efficiency in publicising all these achievements, so that several basic researches in this field, undertaken both in the USSR and abroad, and of fundamental importance for the subsequent development of chemical science, as is now evident, appeared in the journal amost without delay.

Such work included the theory of thermal ignition (N.N.Semenov) and a mathematical formulation for describing thermal flame propagation(D.A.Frank-Kamenetskii), the theory of branched chain reactions, which explains the nature of the lower and upper (pressure) limits of ignition in the oxidation of hydrogen and other elements (N.N.Semenov, C.N.Hinshelwood), and finally direct spectroscopic proof of intermediate formation of the free radical HO· and the determination of its concentration during the oxidation of hydrogen (V.N.Kondrat'ev).

Exceptional progress was made during those years also in formulating theoretical principles of chemical kinetics, with the introduction of such basic concepts as the potential-energy surface and the barrier to reaction. The reader could become acquainted with them from original sources—through review papers by the founders of the theory of rate processes and the transition-state method—H.Eyring, M.Polanyi, E.Wigner, and their successors. Later a special issue appeared in memory of N.A.Shilov, who had elaborated the theory of concerted chemical reactions and made a considerable contribution to the development of several branches of physical chemistry.

Progress in quantum theory, as well as in chemical physics and the kinetics of primary chemical processes, served during those years as a powerful stimulus to elucidation of

the fundamental physical principles underlying chemical changes involving complicated organic compounds. The most significant contributions on this theme were theoretical papers by E.Hückel and by L.Pauling, in which discussion of the structure and the properties of several aromatic and unsaturated organic molecules involved use of molecular orbitals and resonance theory, and also C.K.Ingold's papers ("Principles of the Electronic Theory of Organic Reactions" and "Structure of Benzene"), in which the concept of mesomerism (B.Eistert) was used in posing the same problems. Together with L.Hammett, who published in *Uspekhi Khimii* his review "Some Relations between Reaction Velocities and Equilibrium Constants", which initiated the subsequent widespread use of correlation equations in chemical kinetics (principle of the linear variation of free energy), and in the 1960s introduced the concept of the acidity function H_0 of solutions of strong acids. All the above authors are regarded as founders of the new scientific discipline that was subsequently termed *physical organic chemistry*.

Together with all these trends, research on physical chemistry was also actively pursued during prewar years, and was also exceptionally fully represented on the pages of the journal. This involved physicochemical analysis of salt and colloidal systems, and also of metallic equilibria, the theory of intermolecular forces (G.Briegleb), the theory of melts and solutions (numerous articles on their viscosity and electrical conductivity were provided by V.K.Semenchenko, a collaborator of the journal for many years), the theory of aerosols, adsorption, condensation, evaporation, and vapour pressure. During these and subsequent years the journal reflected in detail the physicochemical interpretation of the photographic process—the theory of the photolysis of silver bromide and formation of the latent image in the emulsion (K.V.Chibisov), optical sensitisation (Kh.S.Bagdasar'yan) and desensitisation, aspects of the mechanism of development, including that of multilayer colour film.

An important direction in which *Uspekhi Khimii* was active in the initial period, which later became traditional, was detailed coverage of the theory and practice of physicochemical methods of investigation and analysis. The journal always appreciated the importance of such contributions, for their conclusions and recommendations were generally promptly used by chemists of the most diverse specialities and have very many practical applications. During the 1930–1940s reviews and papers were published on X-ray structural analysis (W.Bragg), on crystal-optical methods of investigation, dipole moments (N.Sidgwick), the parachor, X-ray diffraction by liquids (H.Stuart), thermotensimetry and calorimetry, ultrasonic methods.

Since many of these methods were at that time relatively novel and not always known to a wide circle of readers, it was important to acquaint specialists with their theoretical basis and practical applications, by publishing papers by their direct originators. This applies to the ultracentrifuge (T.Svedberg), and also to the then recently discovered Raman effect (L.I.Mandel'shtam, G.S.Landsberg), which during those years was used especially widely to establish the structures of organic, inorganic, and polymeric molecules, and also to analyse the hydrocarbons present in liquid fuels. *Uspekhi Khimii* printed also work on molecular spectroscopy (as applied to problems of molecular structure or thermodynamics—Ya.I.Gerasimov), on polarography and chromatography, which subsequently became among the most popular research methods in chemistry and have occupied a prominent place in later issues.

The range of scientific activity of *Uspekhi Khimii* was extremely diverse during those years. The pages reflected organic chemistry (reviews by N.Ya.Dem'yanov and M.Tiffeneau on the novel molecular rearrangements of cyclic hydrocarbon systems with ring expansion and contraction that they discovered), the coordination chemistry of complex compounds (I.I.Chernyaev and A.A.Grinberg's papers), geochemistry (A.P.Vinogradov's papers), the chemistry of hetero-organic compounds—of lithium (G.Wittig), boron and thallium (N.N.Mel'nikov), mercury (A.N.Nesmeyanov), germanium, tin, and lead (K.A.Kocheshkov), and phosphorus (V.M.Plets)—and the chemistry of macromolecular compounds (contributions by H.Staudinger and W.Carothers, its founders), which was especially evident on the pages of the journal during the following decades.

Much of the work published in *Uspekhi Khimii* received high international recognition. Thus physical fields of chemical research or the establishment of novel chemical disciplines were reviewed by winners of the Nobel Prize for chemistry—F.Aston, G.Wittig, O.Hahn, P.Debye, I. and F.Joliot-Curie, W.Lipscomb, I.Langmuir, G.Natta, L.Pauling, W.Prelog, T.Svedberg, N.N.Semenov, G.Seaborg, J.Wilkinson, O.Fischer, G.Hevesy, C.Hinshelwood, H.Staudinger, H.Urey—during various years. Another leading research subject during the 1920–1930s was the chemistry of natural compounds. It is sufficient to state that around ten Nobel Prizes were awarded for work in this field during fifteen prewar years. Most of the winners—A.Windaus (sterols), P.Karrer (carotenoids and flavins, vitamins A and B_2), R.Kuhn (carotenoids and B-group vitamins), A.Butenandt (hormones), L.Ruzicka (polymethylenes and higher terpenes), G.Wieland (cholic acids and oxidative dehydrogenation reactions in Nature)—reviewed their achievements on the pages of this journal. A contributor in 1947 was R.Robinson (research on plant anthocyanins), and later contributors included R.B.Woodward (vitamin B_{12} and development of the chemistry of natural products), A.Todd (nucleotides and coenzymes), D.Crowfoot-Hodgkin (X-ray structural analysis of protein crystals), and quite recently J.Cornforth (biosynthesis of sterols).

The increasing international and All-Union authority of the journal led to the appearance on its pages of papers devoted to several important theoretical studies by major science schools—those of A.N.Frumkin (physicochemical basis of flotation theory and nature of the electrical double layer in electrochemistry), V.M.Goldschmidt (foundations of quantitative geochemistry and principles of the distribution of chemical elements in minerals and rocks), L.Michaelis (semiquinones—intermediate stages in reversible oxidation–reduction involving quinones and hydroquinones), A.Szént-Györgyi (concept of biological oxidation), O.Meyerhof (bioenergetics of muscular contraction), A.N.Bakh (theory of slow oxidation and activation of oxygen in biological systems), and D.Brønsted's theory of acid–base equilibrium.

The great and fruitful editorial experience that had accumulated by the end of the first decade enabled the journal during its subsequent growth to evolve that combination of breadth of coverage of all contemporary chemical literature with depth of insight into physical essence that even in future years will determine the character of much of its contents.

Sometimes the appearance of particular reviews was dictated by contemporary circumstances (e.g. a series of reviews on chemical warfare agents—mustard gas, chloroarsines, lachrymators—and problems of chemical protection), in other cases by the interest taken by the journal in extreme states of matter (chemistry at high temperatures and at high and ultrahigh pressures) and in novel types of action on matter (electric discharge, electric or magnetic fields (E.Müller), ultrasound), or finally simply by day-to-day practical demands, such as reviews on analytical chemistry (radioactive and adsorption indicators (I.M.Kolthoff), organic reagents in inorganic microanalysis (F.Feigl), and

microanalytical advances in studying the composition of minerals and technical products—I.P.Alimarin). During all those years, however, the journal not only followed faithfully the chemical traditions of that time but in several cases was ahead of them or even initiated new ones. By embracing comprehensively almost all the traditional branches of chemistry, many of which, enriched by a physical or physicochemical approach, often evolved into new and independent sciences, the journal served always as a unique methodological clasp permitting the particular scientific interests of chemists of various specialties to be combined into a single whole and conferring on its work a general chemical importance, which it has consistently maintained throughout its half-century history.

Besides its main scientific work *Uspekhi Khimii* paid great attention during all those years to chemical bibliography and the current literature, published many different kinds of information notices and reports (in particular on the activities of science laboratories and institutes of the USSR Academy of Sciences—Institute of General and Inorganic Chemistry, Institute of Organic Chemistry, Bakh Institute of Biochemistry, High-pressure Laboratory—and also on sessions and meetings of the Academy, international scientific congresses, and Mendeleev congresses on general and applied chemistry), and inserted topical notes on various competitions and awards of prizes: i.e. it undertook the great task of informing its readers of the most important events in contemporary chemical science.

Historical and biographical matter also occupied a special place. The journal regularly printed papers and notes on the pioneers of chemical science (M.V.Lomonosov, D.I.Mendeleev, A.P.Borodin, A.B.Bidgeim, M.Berthelot, J.J.Berzelius, J.J.Becher, J.H.van't Hoff, F.Wöhler, J.W.Gibbs, S.Sörensen, H.L.le Châtelier, J.Priestley, J.Thomson, M.Faraday, M.E.Chevreul) and also on eminent contemporary Soviet and foreign academic chemists (A.N.Bakh, A.M.Berkengeim, M.A.Blokh, N.A.Vorontsov, K.K.Gedroits, D.K.Dobroserdov, A.P.Karpinskii, N.S.Kurnakov, A.N.Lebedev, V.V.Longinov, B.N.Menshutkin, V.K.Pershka, N.P.Peskov, L.V.Pisarzhevskii, D.N.Pryanishnikov, A.N.Reformatskii, V.E.Tishchenko, A.E.Favorskii, N.I.Chervyakov, P.P.Shorygin, A.Pictet, J.Ray, M.Sklodowska-Curie, J.Urbain).

The journal published several interesting memoirs (e.g. by P.L.Kapitsa on E.Rutherford, by N.S.Kablukov on the development of chemistry in Moscow University since the 1870s), the historical study by S.S.Nametkin, "Chemistry in Moscow University for 185 Years", and also an analysis of the work of the celebrated International Congress of Chemists at Karlsruhe (1860).

The proportion of articles and reviews of historical and biographical character grew somewhat during the war years, when difficulties in the exchange of world scientific and technical information resulted in a diminished volume of strictly scientific matter, although the journal continued to appear regularly. The editorial board during those years comprised B.M.Berkengeim and V.G.Khlopin (editors-in-chief), A.F.Plate and V.V.Serpinskii (secretaries-in-chief), G.V.Akimov, A.I.Brodskii, A.P.Vinogradov, A.D.Gel'man, B.A.Kazanskii, A.F.Kapustinskii, and A.E.Porai-Koshits. The historical and biographical matter published during the 1940s and 1950s was distinguished by great variety and completeness. Together with biographical information and articles on memorable dates in the history of science, associated with the names of V.F.Alekseev (discovery of the law of the rectilinear diameter), N.N.Beketov, A.P.Borodin, A.M.Butlerov, E.E.Vagner, A.A.Voskresenskii (unknown letter of J.Liebig about him), A.N.Vyshnegradskii and G.G.Gustavson (centenaries of birth), P.D.Dankov, I.A.Dvigubskii (first Russian professor of chemical technology), N.N.Efremov, P.A.Il'enkov (centenary of appearance of *Kurs Khimicheskoi Tekhnologii*), A.A.Colley, D.P.Konovalov, M.G.Kucherov, V.V.Lermantov (author of an early theory of the photographic process), A.A.Letnii (75th anniversary of discovery of the pyrolysis of petroleum), T.E.Lovits, M.V.Lomonosov (bicentenary of his *Slova o Pol'ze Khimii*—"Some Words on Behalf of Chemistry"), V.V.Markovnikov, D.I.Mendeleev, N.A.Menshutkin, N.A.Morozov (scientific forecasts of the well known Schlüsselburger), E.I.Orlov, I.M.Sechenov (chemical work of the Russian physiologist), N.N.Sokolov, L.A.Chugaev, A.El'tekov, and A.A.Yakovskin, as well as A.Werner, B.Clapeyron, A.L.Lavoisier, J.Liebig, the journal continued to print diverse matter also on contemporary scientists (A.E.Arbuzov, G.I.Arbuzov, A.A.Baikov, A.A.Balandin, A.P.Belopol'skii, A.M.Bochvar, E.V.Britske, S.I.Vavilov, V.I.Vernadskii, V.N.Verkhovskii, S.I.Vol'fkovich, N.N.Vorozhtsov, E.N.Gapon, N.Ya.Dem'yanov, A.V.Dumanskii, I.I.Zhukov, Yu.S.Zal'kind, N.D.Zelinskii, S.I.Kanevskaya, V.L.Komarov, V.N.Kondrat'ev, D.P.Konovalov, P.P.Lebedev, S.V.Lebedev, A.I.Loginova, P.G.Melikishvili, Ya.I.Mikhailenko, I.N.Nazarov, S.S.Nametkin, V.A.Nemilov, A.N.Nesmeyanov, B.A.Nititin, B.A.Pavlov, N.P.Peskov, V.M.Petriashvili, L.V.Pisarzhevskii, S.A.Pletenev, A.E.Polesitskii-Yakhnin, A.M.Polyak, A.E.Porai-Koshits, A.V.Rakovskii, P.A.Rebinder, S.Z.Roginskii, V.M.Rodionov, N.N.Semenov, V.K.Semenchenko, M.I.Ushakov, S.N.Ushakov, A.E.Fersman, A.V.Frost, V.G.Khlopin, and I.I.Chernyaev). Furthermore, the journal printed during those years the correspondence of N.N.Zinin, V.V.Markovnikov, A.M.Butlerov, and D.I.Mendeleev (in particular with "supporters" of the Periodic Law—Lecoq de Boisbaudran, Winkler, Nilson, and Brauner), articles on important dates in the history of the discovery of individual chemical elements (argon, ruthenium), on the founder of the nitrogen industry in Russia (I.I.Andreev), and also on the influence of the Kazan chemical school on development of the world chemical industry.

A special issue in 1943 was devoted to the centenary of the discovery of aniline by N.N.Zinin; it included three papers by the eminent Russian chemist and comprehensive biographical material on his life and work. *Uspekhi Khimii* printed other interesting historical studies (e.g. "Some Facts on Chemistry in Armenia from Early Manuscripts"), played an active part in preparations for celebrating the bicentenary of the USSR Academy of Sciences, and, finally, published jubilee reviews on the development in the USSR during the previous 25 years of organic chemistry (A.N.Nesmeyanov), the chemistry of organic dyes and intermediates (A.E.Porai-Koshits), general and inorganic chemistry (A.A.Grinberg), and biochemistry (A.N.Bakh).

Among scientific matter in the journal during the war years were reviews on the chemistry of chlorophyll (by B.N.Stepanenko, who during subsequent years wrote on carbohydrate chemistry in the journal) and on the mechanisms of organic addition, elimination, and substitution (L.M.Smorgonskii), and a fundamental paper on the series rule in analytical chemistry (N.A.Tananaev). During those years the journal followed attentively the achievements of the contemporary X-ray diffractometry and radioscopy of metals, metallic compounds, alloys, and melts; and work on the thermodynamics of solutions at high temperatures, on the application of its achievements to theoretical metallurgy, and on electrokinetic phenomena applied to electrolysis. Other reviews published at that time covered the molecular-spectroscopic analysis of organic compounds, the geochemistry of rare and trace elements in sea-water and the primary migration of radioactive elements in Nature (I.E.Starik),

and also results of and prospects for the coordination theory of A.Werner. Stereochemical matter was not confined to complex compounds (the journal had previously published P.Debye's "Stereochemistry and Physics", H.Hillemann's theory of molecular asymmetry, and M.V.Vol'kenshtein's theory of natural optical activity): interest was extended to internal rotation and rotational isomerism (M.V.Vol'kenshtein). Reviews were published during the war also on the stability of colloidal systems, molecular monolayers on a solid surface, and the role of intermolecular forces of attraction and repulsion in the formation of tactoids, thixotropic gels, and coacervates (I.Langmuir).

The steady interest in such a new subject (at that time) as the chemistry of isotopes requires special mention. As early as the prewar years *Uspekhi Khimii* published a paper by the discoverer of deuterium H.Urey, a fundamental review by F.Aston, who had made several discoveries in this field and had first detected 213 of the 276 then known stable isotopes of chemical elements, and a review by one of the founders of modern radiochemistry G.Hevesy, who had described the first application of radioactive indicators (labelled atoms) to biology. In the 1940s this method had already become one of the main tools of fine chemical research, and the journal helped in all possible ways to disseminate it, having at once published six important reviews, on the use of isotopes of nitrogen, carbon (V.L.Tal'roze, M.B.Neiman), iron (V.I.Gol'danskii, M.B.Neiman), and also deuterium (G.P.Miklukhin) and tritium in chemistry (in the investigation of reaction mechanisms) and in biology. Later, at the end of the 1950s and the beginning of the 1960s, authors providing contributions on radiochemistry were A.N.Murin (thermal diffusion methods for separating isotopes, chemical effects of nuclear reactions in solids), An.N.Nesmeyanov (chemical state of atoms formed in nuclear reactions, hot syntheses of compounds labelled with radiocarbon and tritium, vapour pressure measurements), and V.D.Nefedov (chemical changes in β-disintegration processes, radiochemical methods of obtaining hetero-organic compounds). A major experimental achievement in this field was also the design and accomplishment of a process for isolating more than 100 g of protactinium-231 from residues from the purification of uranium (D.A.Collins et al.).

The stimulation of chemical research, both fundamental and applied, determined the character of the journal in the immediate post-war decade. The extensive series of investigations begun at that time gave rise later to the reviews by A.I.Shatenshtein ("New Work on the Theory of Generalised Lewis Acids and Bases", "Acids and Bases in Liquid Ammonia"), G.A.Razuvaev ("Free-radical Reactions in Tetrachloromethane"), S.I.Vol'kovich ("Progress in Fertiliser Research"), Kh.M.Minachev ("Catalysis in the Hydrogenation of Fuels"), and F.F.Vol'kenshtein ("Electronic Theory of Catalysis on Semiconductors"), all this work being distinguished by the novelty of the theoretical approaches and the up-to-dateness of the experimental methods. The chemistry of natural products was widely represented in the journal at that time in contributions from L.D.Berel'son (steroid hormones, stereochemistry of steroids, chemistry of cortisone), V.M.Berezovskii (vitamins of the B_6 group, pteridines, flavins), N.S.Vul'fson (chemistry of pterins and, later, natural colouring matters), Z.A.Shabarova (structure and synthesis of nucleosides), I.Ya.Postovskii (antibiotics, natural guanidine compounds, antitubercular preparations), and M.M.Shemyakin (vitamins and their inactivators). Other active contributors were A.I.Kiprianov ("Influence of Solvent on Colour of Dyes (Solvatochromism)", "Effect of Steric Hindrance on Properties of Aromatic Amines and Nitro-compounds", "Colour of Dyes and Steric Interference in their Molecules") and A.N.Terenin ("Molecular Compounds and the Intermolecular Electron-transfer Spectrum"), both of whose researches were largely instrumental in converting photonics into an independent branch of science.

A characteristic feature of the work of *Uspekhi Khimii* at that time was unflagging attention to problems of catalysis. Even in its early contents, among which we may note in the first issue an encyclopaedic review by W.Frankenburg and F.Dürr (containing 860 references), it fully appreciated the outstanding value of this branch of science for development of the most diverse fields of chemistry—both its theoretical aspects (physical basis of catalytic reaction mechanisms and theoretical principles underlying the choice of catalysts) and its applied aspects (for the development of up-to-date large-scale catalytic manufactures).

During prewar and postwar years the journal published several important reviews whose authors had shown that the theoretical foundations of the science of catalysis were deeply rooted in the chemical physics and the physical chemistry of heterogeneous and homogeneous reactions (H.S.Taylor's concept of active centres on the surface of a heterogeneous catalyst, K.Weiss's scheme of redox catalysis on transition-metal ions, A.V.Frost's theory of the thermal conversion of hydrocarbons, M.V.Polyakov's idea of hetero-homogeneous reactions, and N.I.Kobozev's theory of active ensembles) and had shed light on the structure and properties of the most important heterogeneous catalysts, problems of the catalytic synthesis of ammonia, and the mechanism of hydrogenation reactions.

Special mention must be made here of the fundamentally important contribution to the work of the journal made by A.A.Balandin, who published in it all his main work—"Catalysis and Change in Form of Molecules", "Catalysis and the Periodic System"—and also a paper on the foundations of his multiplet theory of heterogeneous catalysis on metals, which was most completely formulated in a 1960s two-part paper ("Structural Factors in Catalysis" and "Energetic Factors in Catalysis"). In another contribution to the journal Balandin had raised as early as the 1940s the question of deducing theoretically the complete set of chemical reactions possible for any specified molecular system, and had proposed a special mathematics ("structural algebra") for its solution. This work was one of the first examples of the application, to the analysis of chemical problems, of the logical-heuristic approaches and methods of investigation that are now widely used in organic chemistry, hetero-organic chemistry, and stereochemistry under the general name of *molecular design methods*.

During the 1930s and 1940s contributions in which problems of catalysis were intimately related to those of organic chemistry became especially significant. The general prospects for this approach were outlined in a review by N.D.Zelinskii, A.A.Balandin, and A.M.Rubinshtein, in which catalytic interconversions of saturated, unsaturated, and aromatic hydrocarbons of open-chain and cyclic structure were acknowledged as the main line of investigation.

Hydrocarbon chemistry was very important during those years in connection with the need to solve the problem of obtaining natural and artificial liquid fuel. In *Uspekhi Khimii* these aspects were most widely exposed in a series of reviews by Ya.T.Eidus, who was concerned for a long time with theoretical and applied research on the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide (the Fischer–Tropsch reaction). The journal covered also aspects of the catalytic and contact desulphurisation of petroleum products, regularly acquainted readers with contemporary physicochemical methods of analysis of

hydrocarbon mixtures, and informed them of the most important advances in the processing of petroleum and the production of aviation fuel abroad.

Together with articles summarising the theory and practice of catalytic processes either for particular classes of typical chemical reactions—aromatisation (A.F.Plate), hydrogenation and dehydrogenation (R.Ya.Levina), ring-opening in cyclic hydrocarbons (B.A.Kazanskii)—or for certain types of catalysts (e.g. Raney), the journal regularly included reviews on the chemistry of individual key compounds of enhanced applied value. In the early stages the number of such publications was in general small (e.g. reviews on the use of aluminium chloride in organic chemistry, and also on methanol, pyridine, liquid ammonia, formaldehyde solution, phosphorus, and phosphoric acid). However, such reviews had already become traditional for the journal from the 1940s and 1950s, and covered an increasing variety of compounds.

Articles appeared also on the chemistry of several common large-scale products (gaseous alkanes and alkenes, actylene, butadiene, cyclopentadiene, lower aliphatic alcohols from alkenes, organosilicon monomers, cyanamide, hydrazine, activated carbon) and on new or non-traditional substances and reagents (selenium dioxide, diazomethane, lithium tetrahydroaluminate, new polymerisation initiators, and also boron trifluoride, whose great possibilities as an electrophilic catalyst for alkylation and isomerisation were exhaustively covered in reviews by A.V.Topchiev, Ya.M.Paushkin, and S.V.Zavgorodnii).

We must emphasise also the detailed exposure, typical of the work of the journal at the end of the 1940s and beginning of the 1950s, of progress in the study of several most important organic intermediates and starting materials for fine and special organic syntheses, investigated by the schools of I.N.Nazarov, A.A.Petrov, A.D.Petrov, M.F.Shostakovskii, and V.I.Isagulyants. These were usually unsaturated or difunctional compounds—1,3-dienes and diene esters (and also their halogeno-derivatives), divinyl ketones, pent-1-en-4-yn-3-ols, dienynes, vinyl ethers and sulphides, butadiyne, keten (A.Ya.Yakubovich), 1,3-dichlorobut-1-ene-β-amino-acids (V.M.Rodionov). Several industrially important organic reactions were also given detailed coverage—Kucherov hydration of alkenes (V.N.Belov), formation of oxirans, chlorination of alkenes (studied by N.I.Shuikin's school), alkylation of the aromatic ring (I.P.Tsukervanik), and sulphochlorination of alkanes (A.Ya.Yakubovich), in addition to the nitration of hydrocarbons, the mechanism of which was examined in detail in physicochemical terms by A.I.Titov.

During the postwar period the journal has paid unflagging attention not only to organic synthesis but also to aspects of inorganic and mineral technology. Discussion has covered a wide range of problems in the physical chemistry and technology of glasses, silicates, and spinellides, beginning with contemporary views on their nature (taking into account the contribution to this problem by the I.V.Grebenshchikov school) before examining the kinetics and the mechanism of reactions in solid mixtures (P.P.Budnikov) and specific aspects of glass-making. The journal has paid attention also to problems of thermal reduction methods in metallurgy and of physical phenomena in extrusion and sintering processes in powder metallurgy, and published reviews on the separation of rare-earth elements. Articles by S.I.Vol'fkovich were concerned with the broad task of obtaining compound mineral fertilisers by decomposing phosphates with nitric acid, and also with bringing the teaching of chemical technology up to date.

It must be noted that broadly all reviews on a then important applied subject were characterised by fundamental and diverse coverage of both theoretical and experimental matter, and played an important role in the participation of our chemists in the postwar rehabilitation and development of the chemical industry and the national economy in our land.

The fourth, transitional period in the work of *Uspekhi Khimii* (1950–1960s)¶, which involved preparations for increasing its size (1965), is of great importance for understanding how the present character of the journal has been moulded. It saw further activation of the work of the editorial board, which comprised V.V.Korshak (chief editor), B.M.Berkengeim, S.I.Vol'fkovich, M.M.Dubinin, B.A.Kazanskii, V.V.Mikhailov, B.V.Nekrasov, V.K.Semenchenko, A.M.Sladov (secretary-in-chief), R.P.Lastovskii, Kh.S.Bagdasar'yan, M.I.Kabachnik, and N.M.Emanuel'.

This period was distinguished by considerably intensified development of all chemical sciences. In fundamental research the elaboration and improvement of methods of calculation and computing techniques resulted in great progress in understanding the structure of complicated molecules; such advances as the formulation of theories of perturbations and boundary orbitals, with later discovery of the principle of the conservation of orbital symmetry, paved the way to a deeper insight into the relationship between structure and reactivity. Those years saw the introduction by the experimental chemist of the routine use of such important physical methods of investigation and analysis as nuclear magnetic resonance, mass spectrometry, and also new types of chromatography. The quality of instrumentation also rose considerably during that time. As a consequence of all these factors the traditional sharp division of chemistry into a series of separate classic branches gradually gave way to different, more complicated and significant forms of interrelationship and division between sciences. The major scientific advances and discoveries of those years paved the way for a final shaping of several borderline scientific fields into independent scientific disciplines, among which molecular biology, hetero-organic chemistry, and macromolecular chemistry underwent especially marked development. At the same time stronger demands were made for relevance in scientific research and for a closer relationship with applied, industrial, and technical chemical subjects.

These trends found their organisational expression in the creation of new science research institutes and higher educational institutions, in the founding of new major science centres in several towns. New science schools and lines of chemical research were actively established in those years.

At that time considerable changes were occurring also in the field of chemical information. The total flow of information underwent remarkably strong growth, owing to the inauguration of several new journals and a sharp increase in volume of most chemical publications throughout the world, to an intensification of the issue of monographs, special periodical editions and collections, and to greater activity in the holding of scientific congresses and conferences. In several cases publications exhibited a tendency to narrow specialisation, which might make it difficult to acquaint wide circles of the chemical community with the main trends in contemporary science and prospects for their development.

The profound organisational and structural changes that occurred universally in Soviet and world science during that period posed for the journal the acute problem of working out, under the new conditions, a strategy that would correspond to the greatly increased requirements of specialised chemists for expert and authoritative provision of information. In this situation it was of fundamental importance that the journal should not choose a path of narrow specialisation but,

¶ The silver jubilee of the journal was reported elsewhere[4].

on the contrary, should broaden its interests, by paying attention essentially to the then most promising borderline and contiguous fields of chemical science. As a consequence it is now evident not only that *Uspekhi Khimii* contained the origins of many new sciences initiated in those years but also that its work actively supported their establishment and development.

The most characteristic feature of that time to which the journal responded was the development of hetero-organic chemistry. Just after the war *Uspekhi Khimii* published a paper by A.N.Nesmeyanov on "Hetero-organic Compounds and the Periodic System", which showed results of and the immediate prospects for research on various organic derivatives of metals and non-metals, as well as the important position occupied by this work in the general development of chemical sciences and their interrelationship with various practical requirements and problems. The extremely important role of hetero-organic chemistry in contemporary science was recognised by the creation in 1954 of the Institute of Hetero-organic Compounds of the USSR Academy of Sciences, the first in the world, the work of many of whose personnel on hetero-organic and polymer chemistry, as well as on artificial food, has since been intimately connected with the history of the journal and has appeared in its pages.

These advances were analysed in a 1959 paper by R.Kh.Freidlina, M.I.Kabachnik, and V.V.Korshak included in a special issue celebrating the jubilee of A.N.Nesmeyanov.

The initial growth of this branch of science was due primarily to the development of new methods for obtaining organic derivatives of fluorine, phosphorus, and silicon and was governed by the importance and variety of their fields of practical application. In this connection we may note papers in the journal on methods for introducing fluorine into organic compounds (I.L.Knunyants, O.V.Kil'disheva), on the polymerisation of fluoroalkenes and the addition to them of hydrogen sulphide and thiols, yielding perfluorinated organosulphur compounds (I.L.Knunyants, A.V.Fokin), and also on electrophilic addition to fluoroalkenes (B.L.Dyatkin, I.L.Knunyants), on organofluorine compounds containing functional groups, and on fluorocarbon oils and greases. The chemistry of organic derivatives of silicon was covered by numerous papers by K.A.Andrianov, A.D.Petrov, A.A.Zhdanov, V.F.Mironov, E.A.Chernyshev, and later V.A.Ponomarenko (organofluorosilicon compounds) and also A.B.Topchiev and N.S.Nametkin (organopolysiloxane liquids). The chemistry of organic derivatives of phosphorus appeared during those years in papers by A.E.Arbuzov (organic derivatives of phosphorus acids) and by M.I.Kabachnik (addition of halogen derivatives of phosphorus to organic compounds), and great attention was paid to their biological and insecticidal action (N.N.Mel'nikov).

The journal followed closely the development of the chemistry of organic boron derivatives (U.Lipskii [?W.N.Lipscombe]), regularly publishing for several years reviews on hydroborons (B.V.Nekrasov, Ya.M.Paushkin), diborane, intermediate boranes, borazole (B.M.Mikhailov). It paid attention also the chemistry of new classes of organic derivatives of beryllium, calcium, strontium, barium, and covalent bihetero-organic compounds (N.S.Vyazankin, O.A.Kruglaya), as well as to those of non-metals—the chemistry of cyanuryl chloride, nitrogen-ylides, and phosphorus-ylenes (G.Wittig), cyanohydrocarbons, and compounds containing a nitrogen–fluorine bond (A.V.Fokin).

The vigorous development of the chemistry of σ-bonded organic derivatives of non-metals and non-transition metals (K.Ziegler) was accompanied during those years by great development of a fundamentally new branch—the hetero-organic chemistry of π-complexes of transition metals—which followed on the 1950s discovery of ferrocene and dibenzene-chromium. Its successes were covered in the journal by the reviews of F.Cotton and G.Wilkinson (cyclopentadienyl and arene complexes of metals), G.Wilke (cyclo-oligomerisation of butadiene and π-complexes of transition metals), E.Abel (metal carbonyls), G.A.Razuvaev, V.N.Latyaeva (covalent organometallic compounds of transition metals), and M.I.Rybinskaya, L.V.Rybin (reactivity of a double bond coordinated with a metal atom in nucleophilic reactions). All these early investigations on organometallic π- and σ-complexes paved the way for the subsequent development of metal-complex catalysis in organic and polymer chemistry, which was subsequently reflected on the pages of *Uspekhi Khimii*.

The intense development of synthetic and applied aspects of hetero-organic chemistry in the two postwar decades posed acutely the question of the need to organise systematic quantitative research on the structure and reactivity of hetero-organic compounds and their reaction mechanisms.

During those years the journal responded actively to theoretical questions of hetero-organic chemistry. It was found that organic derivatives of metals and non-metals could serve as new models helping to reveal the physical nature of many chemical phenomena. Thus for several functionally substituted organic derivatives of phosphorus it was possible to elucidate the quantitative laws of tautomeric processes, trace their connection with the principles of acid–base catalysis, and discover on this basis new reactions and rearrangements (M.I.Kabachnik). Articles by O.A.Reutov published in *Uspekhi Khimii* at that time showed that many reactions involving σ-bonded organometallic compounds, in which homolytic transformations are observed with formation of free and latent radicals, may be convenient models for the investigation of radical and chain processes in the condensed phase, and can also be used in hetero-organic synthesis. Finally, detailed examination of the kinetics, stereochemistry, and mechanism of many typical electrophilic reactions (proto- and halogeno-demetallation, alkyl exchange, etc.), precisely on organometallic model compounds (including optically active compounds and those labelled with radioactive mercury-203), enabled quantitative laws to be formulated for electrophilic substitution at saturated and unsaturated carbon atoms (O.A.Reutov) and the broad question to be posed whether the principles of stereochemical dynamics (stereochemistry of substitution in the organometallic series) and statics (the asymmetric non-carbon atom—O.A.Reutov, V.I.Sokolov) could be extended to hetero-organic derivatives of metals and non-metals.

It is significant that, just as in the 1930s the journal had reacted keenly to the development of chemical physics and physical organic chemistry, its contents in the 1950s–1960s directed attention to the physical trend then emerging even in hetero-organic chemistry.

The contents of the journal reflected also segregation of coordination chemistry as a separate field of science at the junction between the organic and the inorganic chemistry of complex compounds. An important role in its development was played by research on the kinetics, stereochemistry, and mechanism of various inner- and outer-sphere reactions of coordination compounds in aqueous and non-aqueous media, and also by R.Nyholm's important generalisation (now known as the Gillespie–Nyholm rule) establishing a direct relation between the electronic configuration and the three-dimensional structure of metal complexes.

Together with the evolution of theoretical ideas on reaction mechanisms involving inorganic and organometallic compounds, great importance was attached at that time to research on the mechanism of purely organic reactions. As reflected in

papers in the journal this involved mainly establishing by correlation analysis quantitative relations between the structure and the reactivity of organic compounds (V.A.Palm) and identifying various intermediate species, the most important of which were carbocations and free radicals (in particular in the nitration of hydrocarbons investigated by A.I.Titov). Later the journal paid great attention also to radical-ion states of molecules (both cation- and anion-radicals), and examined in detail the urgent problem of formation of the antecedent intermediate donor–acceptor complexes and of charge-transfer complexes, which play an important part in the mechanism of such reactions as the addition of halogens to alkenes. Three important reviews were devoted to concerted reactions (Ya.K.Syrkin, J.Mathieu), which involve cyclic electron transfer in closed transition states.

Among the reaction mechanisms investigated in the greatest detail were various acid–base processes (A.I.Shatenshtein), kinetic isotope effects (Ya.M.Varshavskii), including the kinetics and thermodynamics of the isotope exchange of hydrogen, reactions of peroxides, diene synthesis, esterification, hydrolysis of esters (Ya.K.Syrkin, I.I.Moiseev), catalytic redistribution of hydrogen in unsaturated cyclic systems (V.M.Gryaznov), various reactions of isocyanates with compounds containing mobile hydrogen (S.G.Entelis), halogenation of alkenes, and Beckmann rearrangement of oximes (I.L.Knunyants). A series of papers was devoted also to the current problem of the dual reactivity of ambidentate systems (V.I.Erashko, S.A.Shevelov, A.A.Fainzil'berg).

To this day many contributions to the journal on several theoretical aspects of physical organic chemistry have not lost their value, among them reviews by R.Pearson, R.Hudson, A.Parker, J.Edwards, K.U.Ingold, and R.Dessy, in which consideration was given to several contemporary approaches (perturbation theory, principle of hard and soft acids and bases) to the theory of reactivity, and the concepts of basicity and nucleophilicity and the influence of solvation (in particular by bipolar aprotic solvents) on rate, equilibrium, and composition of products in homogeneous reactions were discussed. Several articles appeared also on quantum chemistry, covering the nature of σ- and π-bonds in molecules, the theory of electron shells in molecules (N.D.Sokolov), and principles governing the calculation of conjugated unsaturated systems (M.Dewar).

As before, the most prominent position in the journal was occupied by reviews on chemical physics, in conformity with its great scientific importance. During the period that had elapsed since the beginning of the 1930s many problems had been solved, and the results of all this work had found their place on the pages of *Uspekhi Khimii*. This applies especially to research on the mechanism of gas-phase chain reactions, studied in detail by N.N.Semenov, V.V.Voevodskii, and V.N.Kondrat'ev, the theory of ignition and spontaneous combustion, burning and detonation, and also aspects of the energetics of chemical bonds.

Besides this, establishment of the physical characteristics of primary reactions in the condensed phase became during the 1950–1960s an important problem, investigated for the chain decomposition of halogenated alkanes (N.N.Semenov) and in especial detail for liquid-phase oxidation (N.M.Emanuel'). Additions of inhibitors enabled critical phenomena to be studied, and the possibility of catalysis by salts of metals of variable valency was established (N.M.Emanuel', E.T.Denisov). Elucidation of the mechanism of the action of several inhibitors permitted during those and subsequent years the organisation of a scientific search for and the industrial production of new stabilisers for polymers and various antioxidants, which have great practical value.

As the journal showed, several novel opportunities were offered to chemical physics by the use of new and up-to-date experimental methods, e.g.flash spectroscopy for studying fast photoreactions, chemiluminescence for studying kinetics, vibrational spectroscopy for the structure of polyatomic molecules, and also the method of molecular beams (V.B.Leonas) for elementary chemical reactions. In other cases important results were obtained by developing the theory of chemical kinetics (additive calculation of activation energies, derivation of kinetic equations for homolytic reactions and the temperature dependence of their rates, in some complicated cases taking into account topochemistry and chemisorption processes at the interface). It is evident from the journal that advances in chemical physics contributed much to develop a theoretical basis for contemporary chemical technology, especially in the construction of mathematical models and the search for optimum conditions taking into account the peculiarities of heat and mass transfer in complicated heterophase processes (V.V.Kafarov).

A special number of *Uspekhi Khimii*, issued to celebrate the jubilee of N.N.Semenov, was entirely devoted to the latest advances in chemical physics. Topics covered were investigation of the kinetics and mechanism of branded chain reactions in the gas phase (A.B.Nalbandyan), critical phenomena in degenerate branched chain reactions in the liquid phase (N.M.Emanuel'), current state of the theory of thermal explosion (A.G.Merzhanov, F.I.Dubovitskii), free radicals and chemiluminescence (V.Ya.Shlyapintokh), formation of radicals in reactions of valency-saturated molecules (A.E.Shilov, F.E.D'yachkovskii), chain-transfer reactions with rupture in polymerisation and copolymerisation (N.S.Enikolopov), and chemical reactions at around 77 K (G.B.Sergeev).

Work on high-energy chemistry is near in scientific significance to the above topics, and also has been subject to the constant attention of the journal—ionic and electronic processes in the condensed phase under the influence of radiation (E.L.Frankevich), development of a theory of the primary step in "hot" reactions, various theoretical and applied aspects of the radiation chemistry of aqueous (including frozen) and non-aqueous solutions of organic and inorganic compounds (I.V.Vereshchinskii, A.K.Pikaev, A.J.Swallow).

Thus the work of the journal during the 1950s and 1960s showed that the fundamentally physical direction of chemical research, the results and achievements of which were summarised in the papers "Forty Years of Development of Chemical Physics in the USSR" (V.N.Kondrat'ev) and "Fifty Years of Soviet Physical Chemistry" (N.M.Emanuel'), had succeeded and made it possible to solve the most complicated theoretical and experimental problems by investigating the basic principles of structure and reactivity in chemical compounds.

The third largest sphere of activity of the journal in the 1960s, in addition to hetero-organic chemistry and chemical physics, was the chemistry of macromolecular compounds, whose development was largely governed by the needs of industry and the national economy. A set of reviews on polymer topics was selected by the journal with great care, while the scientific range of the problems covered was extremely varied.

For five to seven years in all the journal dealt creatively with almost every conceivable aspect of this science of great world-wide actuality, beginning with synthesis of the most diverse types of macromolecular compounds—heterochain polyamides (V.V.Korshak, T.M.Frunze), polyarylates, polyacetylenes (A.M.Sladov), polyethyleneimines, polymeric carbonyl compounds, fluorinated organic polymers—discussing the polymerisation possibilities of the most diverse classes of monomers—non-conjugated dienes (G.S.Kolesnikov), iso-butene, polyfluorinated linear compounds, difunctional monomers,

α-oxides—and finishing with the use of physical methods to study various physicomechanical and operating characteristics of macromolecular compounds (gel formation and structure in polymer solutions, electrode properties of ion-exchange membranes, self-diffusion and interdiffusion phenomena (S.S.Voyutskii), as well as the plasticisation of polymer systems, molecular relaxation in polymeric dielectrics, and the chemical action of ultrasonic waves on macromolecules). Special reviews were devoted to the most diverse groups of polymeric substances and materials having great practical value (macromolecular dielectrics and semiconductors (B.I.Sazhin), redox and optically active polymers (I.N.Topchieva), ion-exchange and electron-exchange resins, structural plastics (B.A.Kiselev), and also various kinds of telomers and oligomers). Among other problems discussed were ways of enhancing the frost-resistance and the thermal stability of artificial polymeric materials (M.M.Koton) (including the introduction of cyclic fragments into the polymer chain).

Great attention was paid also to extending the ideas of polymer chemistry to macromolecular systems of natural origin, from organic biopolymers to inorganic systems such as cement and silicates. A series of reviews discussed the chemical modification of macromolecular compounds (e.g. of rubber by vulcanisation or of cellulose by phosphorylation) and indicated the technical prospects of cellulosic ion-exchangers, capable in particular of serving as effective supports in the chromatographic separation of proteins (A.Ya.Nikolaev).

Interesting articles during those years were devoted to the interaction of colorants with macromolecular substances, which was of great importance for development of a textile industry of synthetic fibres, and also to the production of new slow-release medicinal preparations by mixing with macromolecular fillers or by grafting to polymer chains.

In several cases the journal has even arranged series of reviews on related topics, if the problem involved deserves that the gap should be urgently filled with consequent stimulation of its development. For inclusion in such series only those reviews are selected, of course, that give independent and expert views without duplicating general information on the subject. An example is the publication over only a few years of about ten reviews covering the most diverse aspects of the main subject "Macromolecular Hetero-organic Compounds", then especially timely. By surveying both purely inorganic systems as a whole (H.J.Emeléus) and also polymers having inorganic main chains (K.A.Andrianov, A.A.Zhdanov), with a discussion of hetero-organic systems, as well as coordination polymers and polymeric chelates, the journal gave within a short period a very complete picture of the state of this branch of science throughout the world in the 1960s.

Examination of the work of the journal on electrochemistry reveals firstly a steady growth in the total number of contributions on this important discipline and secondly an unusual list of review topics in past and present years, reflecting the chief changes in the theoretical and applied content of this extremely broad and diverse branch of science.

Electrochemical matter in *Uspekhi Khimii* during its first two decades was primarily associated with the name of A.N.Frumkin, who as early as 1935 contributed his well known review on the nature of the electrical double layer in electrochemistry (a general analysis of his publications will be found in a 1941 paper by N.A.Bakh). The former followed with his reviews on surface adsorption phenomena in electrochemical oxidation and reduction, on the electrochemistry of protective films (together with G.V.Akimov), and also on electrochemical kinetics, aspects of which were discussed also in contributions by S.Glasstone and by N.I.Zhukov (as applied to electrodialysis).

During subsequent years these questions were further developed on the pages of the journal by the work of Frumkin's students and followers (a special number of *Uspekhi Khimii* was dedicated to him in 1975). This comprised primarily a detailed account of a wide range of topics in the theory of the electrical double layer (B.B.Damaskin) at the boundary between an electrolyte and various electrodes (including those based on bismuth, tin, cadmium, and lead (U.V.Palm, V.E.Past), for all of which the influence of the crystallographic structure of the solid surface was examined, and also that of specific interaction of the surface with the solvent, on the properties of the double layer, the adsorption of ions, and the kinetics of hydrogen evolution in acid and alkaline media). Most of the reviews on this subject gave the most detailed consideration to mercury and platinum electrodes, study of which, in particular, made use of a radioactive tracer method that had been employed also to examine solid electrolytes (S.V.Karpachev, Yu.Ya.Gurevich) and non-aqueous media. The great interest taken by the journal in electrochemical processes in non-aqueous solvents (a special article on this topic as early as 1948 was devoted to the work of L.V.Pisarzhevskii's school) was due to the frequent possibility of controlling in them the progress of the proton-transfer processes accompanying electron transfer, which produces favourable conditions for electrometric analysis—electrochemistry of chelates in non-aqueous media (G.K.Budnikov), polarography in organic solvents (S.I.Zhdanov).

Surface adsorption phenomena, whose study is important both from the general physicochemical viewpoint and for an understanding of the mechanism of ensuing electrode processes and the laws of electrochemical kinetics, were covered in detail by the reviews of B.B.Damaskin (laws of the adsorption of organic compounds) and of O.A.Petrii (adsorption of electrodes of platinum-group metals), which gave a thermodynamic theory of the platinum electrode. Great attention was paid by the journal also to the kinetics and mechanism of electrochemical reactions, as well as the nature of unstable intermediate species. Apart from papers on electrometry and electrosynthesis, which will be named below, this range of problems was considered in relation to the most diverse systems—from metal ions in unusual and unstable states of oxidation (B.G.Ershov) and metal complexes in aqueous electrolyte solutions (V.I.Kravtsov) to molecular oxygen (L.I.Nekrasov) and semiconductors—kinetics of chemical etching, formation of new phases (V.A.Myamlin, Yu.V.Pleskov). Of great value for an understanding of several pressing problems of theoretical electrochemistry were the papers of B.V.Ershler (problem of absolute potential), G.A.Tedoradze and A.B.Ershler (effect of large coverages), and also R.R.Dogonadze, A.M.Kuznetsov, and L.I.Krishtalik, on theories of electronic processes in liquids, barrierless electrode processes, and also the nature of the primary step in electrode reactions.

The journal has always associated theoretical aspects of electrochemistry closely with practical applications, among which the greatest attention is now paid to three vast fields—the development of classic and new methods for the electrometric analysis of inorganic and organic compounds, preparative electrolysis and electrosynthesis of organic and mineral substances, and also problems of the corrosion of metals and alloys.

Uspekhi Khimii has at different times published papers both on equilibrium and on non-equilibrium methods of electrometric analysis (with application of a potential or passage of

a current), the interrelationship between which has been considered in greatest detail in I.M.Kolthoff's well known review "Relation between Potentiometric and Amperometric Titration and Voltammetry". During recent years the journal has given space to especially detailed consideration of the possibilities of the polarographic method of investigation and analysis, both of inorganic systems (e.g. ions of bivalent iron, cobalt, nickel—V.N.Pavlov, V.V.Bondar') and their chemical reactions (e.g. study of equilibrium complex formation—S.I.Zhdanov), with redoximetry for interactions in solutions (V.V.Pal'chevskii), and of various hetero-organic (S.G.Mairanovskii) and organic compounds—cathodic reduction of benzenoid aromatic hydrocarbons (S.I.Zhdanov), coumarins (Yu.E.Orlov), and aminoalkyl esters of αβ-unsaturated acids, and also study of the reactions of carbonyl compounds with ammonia, including their use in polarographic analysis (Ya.I.Tur'yan). The journal has also covered such methods as oscillopolarography and extraction polarography (G.K.Budnikov), inversion amalgam chronopotentiometry (V.I.Bakonov, M.S.Zakharov), and also thin-layer electrochemistry (S.I.Zhdanov). Electrochemical processes produced by alternating currents have also been discussed (impedance method—B.M.Grafov, E.A.Ukshe). Among new electrochemical achievements reported during recent years have been ion-selective electrodes (A.A.Belyustin), opening up several opportunities for investigating complicated enzyme systems involving choline esterases, and also the photoemission of electrons from metals in electrolyte solutions (Yu.V.Pleskov, Z.A.Rotenberg).

Electrochemical methods of investigation, based on a common treatment of acid–base and redox processes under homogeneous and heterogeneous conditions, are now widely used in solving a wide range of problems of physical chemistry and related disciplines. This important trend, whose earlier development was evident in the contributions by V.A.Pleskov (electrode potentials and ionic solvation energies) and by S.S.Voyutskii (electrokinetic potential as measure of aggregate stability of disperse particles), is now represented by the papers of A.Ya.Gokhshtein (elastic method for the study of various surface phenomena), and of R.Sh.Nigmatullin et al. (electrochemical investigation of mass and momentum transfer in solid–liquid systems, electrochemical modelling of heat and mass exchange, and also several hydrodynamic characteristics).

Important practical applications of electrochemical research results are associated in the journal with preparative electrolysis and electrosynthesis. The electrodeposition and electrocrystallisation of metals, surveyed in the 1950s by V.V.Mikhailov and by L.I.Antropov, were subsequently developed in papers on electrolysis at a mercury cathode as a method of isolation of uranium and separation of rare-earth elements (G.M.Kolesov). Several general problems of the electrolysis of molten media (surveyed by A.I.Belov in connection with the 150th anniversary of this method) have been examined in detail for oxide (A.M.Samarin) and hydroxide (O.G.Zarubitskii) melts. Together with inorganic systems (electrochemistry of iodine, selenium, tellurium, as well as metals and their complexes) the journal has always taken great interest in the electrosynthesis of organic compounds, first discussed by N.N.Mel'nikov as early as the 1930s and then by M.Ya.Fioshin in the 1950s. Recent reviews (M.Ya.Fioshin, A.P.Tomilov, L.A.Mirkind, I.N.Rozhkov) show that modern trends in development involve primarily expansion of the range of cathodic and anodic reactions initiated by electrochemical methods. Thus detailed studies are now being made of the oxidation of organic compounds at transition-metal oxide anodes, electrochemical alkoxylation and anodic dimerisation, addition, and substitution, and also cathodic coupling and electrolytic reduction of multiple bonds. A series of papers covered the mechanism of electrosynthetic processes involving organic compounds, the role of free radicals in electrolysis, reactions of these species with the electrode material, and also the cation–radical mechanism of anodic fluorination.

In addition to electrometric analysis, electrolysis, and electrosynthesis an independent and very important field of practical application of electrochemical knowledge is the mechanism and prevention of corrosion. The corrosion of metals as a special problem of colloid electrochemistry was first raised in the journal by V.A.Kistyakovskii as early as 1933 (later, outlines of the achievements of his scientific school were published in *Uspekhi Khimii* in 1945 and 1951). The bulk of the contributions on this theme belong to the 1950–1960s, when the journal published within a short period a whole series on the chemical nature of the corrosion and protection of metals from most diverse external attacks (atmospheric, subterranean, and pitting corrosion, as well as by sea-water at the water-line, or under conditions of limited access of electrolyte). A characteristic feature of this work is the discussion of ways for improving the corrosion resistance of metals and alloys in terms of the electrochemical theory of corrosion (N.D.Tomashov), including the theory of multielectrode systems (G.V.Akimov). The wide and up-to-date coverage of the whole set of most complicated questions associated with corrosion, in whose investigation radioisotope methods were used earlier, and also the influence of anions on the kinetics of dissolution of metals (Ya.M.Kolotyrkin), shows the great value attached by the journal to this important problem of applied science.

While attaching great importance to applied aspects of macromolecular chemistry, all that time the journal never lost sight of fundamental problems of general scientific and theoretical character in this field. Several reviews in those years were devoted to such questions as kinetic features of primary stages in polymerisation and further chemical reactions of the macromolecular compounds, mechanisms of interfacial polycondensation and ionic telomerisation, as well as free-radical, ionic [cationic (L.S.Bresler) or anionic], radiochemical, and cyclic polymerisation and copolymerisation of the most diverse classes of monomers under various experimental conditions, in several cases drawing special attention to novel, unusual, or anomalous types of reactions.

The journal has also extensively published many reviews and papers on general aspects of polymer chemistry—on progress in studying the chief types of processes in polymer formation (e.g. non-equilibrium and equilibrium polycondensation (V.V.Korshak), polymerisation of chemically activated monomers—V.A.Kabanov), on the main lines of research on polymer structure (e.g. the role of structural phenomena in shaping their properties—V.A.Kargin) and study of their reactivity (A.A.Berlin)—indicated future prospects for development in this field of science (reviews by M.Szwarc on "Progress in Polymers" and by H.W.Melville on "Future of Polymer Science"), and acquainted the reader—from original sources, as always—with the story of the major scientific discoveries ("Advances in Stereospecific Polymerisation" by G.Natta). This group can be completed by two articles—"Nomenclature of Linear Polymers based on their Structure" and "Nomenclature of Stereoregular Polymers" (H.Mark)—which have proved extremely useful in bringing the fairly intricate systematisation of complicated three-dimensional polymer structures into harmony with international requirements.

Uspekhi Khimii always reacted so keenly and originally to the conception and establishment of new scientific disciplines, to their differentiation, specialisation, and integration, that its reviews could form the basis of an objective and accurate view both of the origin of most of the most recent branches

of chemistry and of the current trends in their development. It is instructive in this connection to consider e.g. the dynamics of qualitative and quantitative changes in character of reviews in such an important field of applied science as adsorption (M.M.Dubinin), colloid chemistry (B.V.Deryagin), and chromatographic analysis.

With regard to the review activity of the journal on chromatographic analysis, there was a time when practice in this field clearly lagged behind theory. Although in the 1930s great progress was made in understanding the nature of adsorption bonding, heats of adsorption, and the work of adsorption forces (A.V.Kiselev), chromatographic methods of separation and analysis had not yet been properly developed.

At the beginning of the 1940s, however, major scientific developments—A.Martin and R.Synge's improvement of M.S.Tswett's adsorption chromatography and the elaboration of convenient methods of partition chromatography—and also the discovery in the 1950s of methods of column and capillary gas–liquid chromatography led to an immediate intensification of research in this field. The number of reviews on this subject in the journal increased by a factor of several tens, and they themselves came to acquire a differentiated character. Separation of the subject-matter of scientific and applied investigations took place in several directions. Thus paper chromatography (V.V.Rachinskii) became an individual subject, while partition chromatography was so greatly perfected that its application to analytical (N.N.Fuks), inorganic (E.N. and T.B.Gapon), organic, and biological (V.S.Asatiani) chemistry acquired independent significance according to the character of the substances to be separated and analysed.

Subsequently (in the 1960s) a tendency to still more far-reaching and detailed specialisation of individual types of scientific and practical chromatography began to appear, further subdivision of which began at once on three or four planes depending both on the chromatographic method and on the nature of the mixtures of gaseous (A.A.Zhukhovitskii and N.M.Turkel'taub), inorganic, organic, or natural substances to be separated or analysed. Special reviews were now required both on individual types of sorbents (e.g. ion-exchange celluloses, separation of biopolymers on calcium phosphate gels, or asymmetric adsorption as a method of resolving racemates on dissymmetric sorbents—S.V.Rogozhin, B.A.Davankov) and on the types of substrates to be separated (e.g. in the case of organic compounds comprehensive data were accumulated on the chromatographic separation of liquid petroleum hydrocarbons and individually on compounds of the benzene series, and matter on biologically active polymers came to be subdivided into separate reviews on the separation of mixtures of amino-acids (V.M.Belikov), lipids, carbohydrates, nucleic acids and their components, and decomposition products of proteins). Chromatographic methods became increasingly valuable for analysis and separation [?omission, Ed. of Translation] (including as volatile complexes), and also of Groups I–IV organometallic compounds (K.I.Sakodynskii).

In the current stage the coverage of chromatography by *Uspekhi Khimii* is governed by three principal stimuli—firstly further improvements in instrumental chromatographic technique, secondly introduction of several fundamentally novel forms of chromatographic analysis, and thirdly significant expansion of areas of practical use of these methods in the most diverse scientific and applied fields—so that only during recent years has the journal published reviews on the theory of the chromatographic microreactor, the use of packed capillary columns, chromatographic analysis with temperature programming, pulsed and high-temperature chromatography, chromatography in a stream of water vapour, gas chromatography with organic eluants, and also high-pressure gas and liquid chromatography (M.S.Vigdergauz). Newly introduced methods of chromatographic separation and analysis, whose establishment is attentively followed by the journal (peak paper chromatography, ion-exchange, precipitation, reverse, affinity, electrolytic, and gel chromatography), are subject in several cases to a tendency to undergo further differentiation. Thus within the scope of the promising method of reaction chromatography several variants have appeared, e.g. chemispecific covalent chromatography (S.V.Rogozhin) or adsorption–complexing chromatography, in particular involving the formation of charge-transfer complexes.

At the same time a vigorous world-wide search is now being made for new carriers, mobile and stationary phases (in particular surface-film sorbents), and in recent years the journal has drawn attention to the use for this purpose of liquid-crystal systems (gas–liquid-crystal chromatography, and also adsorption–absorption chromatography on Silochromes having films of liquid crystals). Another trend that can be observed in recent issues is the contrary tendency to integrate separate scientific disciplines at new and higher levels, which is evident e.g. in the active penetration of chromatographic methods into adjacent scientific fields for the solution of such problems as the determination of thermodynamic interpretation of the concepts of the polarity and the selectivity of sorbents, for the study of problems in catalysis and polymer chemistry, for investigation of the kinetics of liquid-phase reactions and the state of the multivalent ions in solution, and for the functional analysis of organic compounds (V.G.Berezkin et al.) and of unstable inorganic and heteroorganic species, quite apart from the analysis of trace impurities, atmospheric pollution, etc.

Since reviews on the development of a general-purpose chromatographic method are, very likely, of the greatest interest literally to all experimental specialists in chemistry and chemical technology, the above examples confirm how closely and effectively the journal has followed the most advanced attainments of scientific and technical ideas, and has responded to the continual interchange between the enrichment of various fields of chemical science and practice.

With regard to the modern period in the work of *Uspekhi Khimii* it must be remarked that the present stage in the development of chemical science is indeed characterised by an avalanche of primary information with simultaneous increase in its complexity and saturation. Monographs and textbooks are often unable to react promptly to such developments in various areas, and therefore delay considerably the dissemination of information to chemists in comparison with the periodical literature. This makes the work of chemical review journals especially valuable.

Furthermore, a modern review journal cannot allow itself simply to inform the reader on new scientific achievements: it should serve as a reliable guide in the flux of scientific trends and, by actively directing this process, form a fine structure of contemporary scientific knowledge. By making good the informational deficiency on the most important and urgent scientific questions, while actively moulding the reader's taste and providing a system of contemporary chemical values and priorities, *Uspekhi Khimii* by its practice of strict selection and commission of primary reviews exerts a necessary controlling and organising influence on the very course of the informational process, often foreseeing important tendencies in current and future chemical progress.

The methodological basis of the journal remains as before, as also fifty years ago, to publish contributions on chemical physics, whose importance in modern science is continually increasing. The main prospects for development in

experimental chemical physics, in the opinion of N.N.Semonov expressed in his recent address to an International Symposium on Chemical Physics (Moscow and Erevan, 1981)[5], are governed by a combination of possibilities of the modern theory of primary chemical processes with the use of new experimental physicochemical methods of investigation, among which special value attaches to those that allow appropriate reagents and products to be specified in definite quantum states (electronic, rotational, spin) and thereby the microscopic rate constants of primary reactions and energy-exchange processes to be found.

It is precisely these aspects of chemical physics (both theoretical and experimental) that the journal has been covering during the modern stage. Concerning the theory of primary chemical processes and chemical kinetics (an important part in the establishment of these domains was played by V.N.Kondrat'ev and V.V.Voevodskii, in whose memory special issues were published) the journal has contained during recent years reviews on the current state of the theory of bimolecular reactions, the mechanism of non-adiabatic bimolecular reactions and non-adiabatic energy transfer in gases (E.E.Nikitin), and the nature of the pre-exponential factor in the rate equations of unimolecular gas reactions and hydrogen-abstraction reactions. In addition, the kinetics of molecular reactions, the theory of complicated unimolecular reactions, molecular and kinetic aspects of the chemical physics of the condensed state and reactions in solid polymers (P.Yu.Butyagin), and dynamic primary processes in liquids have been discussed, quantitative appraisals of the mechanism of several reactions of hydrocarbons given, and finally the kinetics of homogeneous reactions in a vessel with ideal mixing (open systems) described (N.M.Emanuel').

Several articles have been devoted to the use of correlation equations in the kinetics of free-radical reactions, and also to questions of the separation of polar, steric, and resonance effects in organic reactions on the principle of the linearity of free energy changes (this same principle has been used also to analyse and summarise extraction data).

Reviews of experimental work continue to pay attention mainly to the kinetics and the mechanism of homolytic processes, having discussed the formation of radicals in the devitrification of matrices, the mutual interaction of atoms and radicals in the liquid phase and their redox reactions with ions in solution, the reactivity of radicals and molecules in various radical reactions (including ternary recombination processes, and also in the solid phase—in connection with the mechanism of the oxidation of carbon-chain polymers), and finally reversible recombination and redox reactions of radicals (I.V.Khudyakov, V.A.Kuz'min).

A number of articles have shown that research on radicals and their reactions now makes use of the great variety of physical methods—electron spin resonance, nuclear magnetic resonance and chemical polarisation of electrons and nuclei (A.L.Buchachenko), chemical lasers (to determine rate constants of reactions of atoms with molecules and the relaxation of vibrationally excited molecules), flash photoexcitation (A.K.Chibisov—to investigate triplet states of organic substances), and finally isotope and mass-spectrometric methods in solution, as well as the method of spin traps (*inter alia* to study radical species containing chlorine or sulphur).

A major achievement here was the discovery of the influence of a magnetic field on radical reactions in solution (R.Z.Sagdeev, K.M.Salikhov, Yu.N.Molin, A.L.Buchachenko).

During the past decades *Uspekhi Khimii* has paid especially close attention to the chemistry of excited states of substances. This subject has been covered by reviews on mechanisms of excitation of chemiluminescence, mechanisms of reactions of electronically excited radicals and quenching of excited states of radicals, primary photoionisation processes and ion–molecule reactions of organic substances (including those induced by β-disintegration of hydrogen-3 in tritiated compounds), photoreactions of free radicals in the solid phase (the nature of the primary photochemical step was examined by K.M.Dyumaev), and proton-transfer reactions in electronically excited aromatic molecules (M.G.Kuz'min).

Research workers have now become very interested in catalytic and photoinduced electron transfer (and also the tunnel transfer of an electron to great distances), photoinitiated reactions of quinones and the photoreduction of aromatic nitro-compounds, radiation-induced electronic processes in solid organic systems, and the investigation in such systems of primary chemical reactions due to the formation of radical-pairs. Understanding of the mechanism of formation of free radicals in the liquid-phase halogenation of alkenes has been facilitated by the concept of intermediate formation in them of corresponding donor–acceptor molecular complexes.

Several papers in the journal have been concerned with fundamental aspects of high-energy chemistry—problem of the solvated electron in polar organic and non-polar molecular liquids (A.V.Vannikov), influence of impurities on radiation-chemical processes in inorganic salt crystals (V.V.Gromov), action of radiation on dissolution, and also the kinetics of chemical reactions initiated by hot atoms and the chemistry of hot (1–3 eV) hydrogen atoms.

The current interest of chemical physics in radical processes is due in particular to their use in the hydroxylation of aromatic compounds and the direct epoxidation of alkenes in the liquid phase (D.I.Metelitsa), as well as in subsequent chemical reactions of epoxy-compounds. However, the main value of such reactions lies in the oxidation of the most diverse classes of organic compounds—benzene (E.T.Denisov, D.I.Metelitsa), alkylaromatic hydrocarbons, alkenes, cycloalkenes, and aldehydes, for which the kinetics and reaction mechanisms have been studied, in particular the role of steric factors and spatial strain of the double bond.

Parallel development is occurring in study of the chemical and chemicophysical properties of oxidants—molecular oxygen and its radical-anion O_2^- oxygen activated by transition-metal complexes, singlet oxygen (its formation, quenching, chemical properties, and value in biological systems), and also the reactivity of the oxygen-containing radicals $HO^\cdot$, $O^\cdot$, $HO_2^\cdot$, and atomic oxygen (V.Ya.Shlapintokh, I.B.Afanas'ev, V.B.Aleskovskii) (results of and prospects for study of $HO_2^\cdot$ have been covered in the greatest detail in view of the contributions by V.V.Voevodskii).

Theoretical work of the preceding years (much of which also has been published in *Uspekhi Khimii*) has shown that a fundamentally important stage in the mechanism of many liquid-phase oxidations is degenerate chain branching, in which molecular products of the primary chain reaction (in the autoxidation of hydrocarbons these are hydroperoxides) can in turn act as initiators of further chain reactions. Subsequent development of this branch of chemical physics has involved detailed investigation of individual stages in liquid-phase oxidations, mostly by modelling them in specially selected reaction systems (E.T.Denisov, D.B.Pobedimskii). Thus intensive research has been undertaken on the primary reactions of oxidation inhibitors, whose role is either chain termination by reaction with alkyl radicals (nitroxyl and quinone inhibitors) or peroxy-radicals (amine and phenolic inhibitors) or non-radical decomposition of the accumulating hydroperoxides (I.V.Khudyakov, V.A.Kuz'min). Reviews in the journal have shown that these two types of reactions are modelled e.g. by the interaction of known hydroperoxides (as well as $PO^\cdot$, $PS^\cdot$, $PO_2^\cdot$ radicals) with sulphides, phosphines, and aromatic amines (D.G.Pobedimskii) and by the oxidation of sterically hindered phenols and amines. The kinetics

and the mechanism of the breakdown of hydroperoxides in the presence of transition-metal compounds and the metal-catalysed oxidation of organic compounds by hydroperoxides are also being investigated (G.A.Tolstikov, V.P.Yur'ev, U.M.Dzhemilov). Association in alcohols and phenols has been studied by nuclear magnetic resonance (V.D.Pokhodenko). All these current lines of research, represented in detail in the journal, are important for an understanding of the main features of the mechanism of inhibited oxidation, for a scientifically based search for new inhibitors and antioxidants, and for the study of synergism in their action in composite materials. An important part has been played by posing in the journal the question whether selectivity in chemical reactions is not a kinetic problem (N.M.Emanuel').

All work on the chemical physics of oxidation, among which an important position is occupied by investigations of the aging and the stabilisation of polymers, and also the kinetics of their degradation (*inter alia* in aggressive liquid media), is directly related to the most important practical problem of the protection from oxidation of several artificial and natural materials—fuels, lubricants, oils and fats [the problem of studying physicochemical mechanisms of damage to DNA is raised in the work—by means of various types of synthetic oxidation inhibitors and bioantioxidants (which include chemical geroprotectors)]. The great interest taken by the journal in such questions is indicated by its gathering together in one issue reviews on allied topics, in which the task of predicting changes in the properties of polymer materials on prolonged storage and service (including polyalkenes on photo-oxidation), and also measuring their durability and service life, was treated as a general physicochemical problem, whose solution could be facilitated by the construction of appropriate kinetic models. By using such interrelated series of publications to direct the attention of the reader to matters of great scientific and applied importance, *Uspekhi Khimii* is in some measure following the practice of another of our review publications—*Zhurnal Vsesoyuznogo Khimicheskogo Obshchestva im. D.I.Mendeleeva* [Journal of the Mendeleev All-Union Chemical Society] (published since 1956), every number of which is devoted to the subject-matter of a single major problem.

During recent years *Uspekhi Khimii* has published, besides reviews on the above scientific trends, several contributions on the chemistry of the positron, the muon, and mesoatoms (V.I.Gol'danskii, V.G.Firsov), the physics and chemistry involved being studied even in complicated polymer systems. The positron method enables the effective charge on anions in ionic media to be determined, and also new results on the structure of materials to be interpreted in the light of the Periodic Law (V.I.Gol'danskii). Several studies have appeared on novel physical actions on matter—processes occurring in solids under the influence of shock waves (A.N.Dremin), changes in condensed substances on shock-wave compression under controlled thermodynamic conditions (V.I.Gol'danskii), and epitaxial production of diamond in the metastable region (B.V.Deryagin, D.V.Fedoseev). Consideration has been given also to the formation of organic surface films by an electron beam, ultraviolet radiation, and a glow discharge, as well as the production of high-temperature materials by direct high-frequency melting in a cold container.

The classic problems of chemical physics—the theory of ignition, combustion, and explosion—first covered by the journal as early as 1930s, are now undergoing development. The present interests of research workers lie in using mass spectrometry to study flame structure and burning processes, in studying the thermal decomposition of aliphatic *C*- and *N*-nitro-compounds, and in the possibilities of practical application of the results to chemical technology and metallurgy (F.I.Dubovitskii, A.G.Merzhanov). The completeness of coverage of modern scientific trends in study of the physical foundations of chemical science is shown also by articles on the chemistry of low and extremely low temperatures associated with the phenomenon of a low-temperature quantum limit to the rate of chemical reactions (V.I.Gol'danskii), on solid-state chemistry (V.V.Boldyrev, P.Yu.Butyagin) (kinetics and nature of mechanochemical reactions, mechanism and kinetics of the dehydration of crystal hydrates), and on the classic thermodynamics of isotope exchange (N.M.Zhavoronkov).

The activity in publicising the fundamental physical foundations of chemical processes is especially important at the present stage in the work of the journal also because it is knowledge of the physical principles underlying the structure and the reactivity of various classes of compounds that is of the greatest interest to the majority of readers. Despite the organisation and publication during recent years of a multitude of sectional and interdepartmental review symposia, and also the active participation of many specialised chemical journals in review work, *Uspekhi Khimii* continues to play its part of general chemical review publication, reflecting not only the specialisation and differentiation occurring in chemical sciences but also the considerably more complicated contrary processes of mutual integration with the formation of new major fields of science.

Especially significant in this respect is the great attention paid to enzyme chemistry, a fundamentally new and important trend in the activity of the journal during the past decade. On this subject *Uspekhi Khimii* by no means publishes work on the structure of individual enzymes (which is the concern of specialist journals) but focuses its attention on reviews of general character, of interest to wide circles of specialists. At the present time it appears from the contents (I.V.Berezin, K.Martinek) that the main interest lies in the problem of enzymatic catalysis, for whose solution the methods of chemical kinetics and thermodynamics are widely used (in particular in study of the nature of intermediate compounds). Apart from its theoretical significance this type of catalysis has recently acquired immense applied importance, and now the chief problem is to stabilise enzymes, a key factor in the introduction of biocatalysis both into industrial practice and into organic synthesis. This many-sided research is directed mainly at immobilising enzymes, especially by the use of polymeric carriers. In sum, all this work draws attention to a new and independent branch of science, development of which will stimulate growth in all related theoretical and applied disciplines and promises major advances in the near future.

At present the most promising direction in the search for new catalysts—chemical bionics—involves chemical modelling of the action of enzymes (primarily lysozyme, which effects biocatalytic hydrolysis (V.I.Maksimov), as well as cytochromes, oxygenases and nitrogenases, responsible respectively for the anobolism of atmospheric oxygen and nitrogen *in vivo*). A convincing advance in this field is the discovery of new nitrogen-fixing systems based on vanadium in a low state of oxidation, which operate in aqueous solutions at ordinary temperatures and pressures (A.E.Shilov). Another modern line of research (bioinorganic chemistry), at the boundary between biochemistry and the coordination chemistry of physiologically active oxygen-, nitrogen-, and sulphur-centred ligands, is also represented in reviews, on chlorophyll, its synthetic analogues, metal porphyrins, and also the interaction of metals with nucleic acids (E.E.Kriss, K.B.Yatsimirskii) and proteins (V.A.Sergeev, M.G.Bezrukov). Yet another direction of advance (bioheteroorganic

chemistry) is apparent in papers on establishing the nature of hydrophobic sites on the active surface of choline esterases and of the mechanism of their inhibition by organophosphorus compounds (M.I.Kabachnik, N.N.Godovikov, M.Ya.Mikhel'son, A.P.Brestkin, Vi.I.Rozengart, et al.).

The journal has always paid great attention to the three-dimensional structure of complicated molecular systems, both by publishing special reviews on stereochemistry and conformational analysis (anomeric effect, stereospecific synthesis and catalysis, asymmetric synthesis of α-amino-acids, planar chirality of metallocenes, stereochemistry of hydroxymercuration, transannular effects in macrorings and *p*-cyclophanes) and by discussing various types of steric and spatial effects in a considerable number of the most diverse studies. As early as the 1960s the journal opportunely discerned the permeation of classic stereochemistry by several novel and fertile trends ("Algebraic Aspect of Chirality" by E.Ruh, "Problems of Chemical Topology" by W.Prelog, "Topological Ideas in Stereochemistry" by V.I.Sokolov) promoting an understanding of spatial relations in the molecular world. During recent years a close interest has been taken in framework and polyhedral structures—adamantanes and their hetero-analogues, the problem of tetrahedrane (N.S.Zefirov), carboranes and their rearrangements (L.I.Zakharkin, V.N.Kalinin, V.I.Stanko, V.I.Bregadze)—and a clearly structural approach characterises matter on the theory of cyclisation–recyclisation processes and also on structural aspects of several solid-phase reactions and rearrangements (right up to polymerisation processes).

Modern in both content and form is a recent review by V.I.Minkin and R.A.Minyaev on "Polyhedral Organic Molecules and Ions—Structural Analogues of Organometallic Clusters", which uses current orbital ideas and R.Hoffman's principle of isolobality to show the possibility of a single approach to understanding the fundamental interrelations between organic and hetero-organic compounds. A feature of this work is a general and fruitful analogy revealing interrelations between different branches of chemistry, unexpected at first glance but capable of serving as a guide to further experimental and theoretical investigations.

New stereochemical ideas are finding application also in practical chemistry. For example, several reviews in the journal explain catalysis on zeolites by the enclosure of reactant molecules in cavities bounded by the aluminosilicate framework (Kh.M.Minachev), and the molecules of inorganic heteropoly-acids have a different but also very complicated three-dimensional structure (V.I.Spitsyn); catalysis by cyclodextrins is attributed also to the presence in their spiralled molecules of a special kind of cylindrical cavity surrounded by polysaccharide chains. In the molecules of macrocyclic crown polyethers, which now play a very important part in the most diverse branches of chemistry (K.D.Pedersen), the appearance of coordination vacancies for particles of suitable size (e.g. metal ions) is also due to a peculiarity of the spatial structure of the cyclic multidentate ligand. Complexes formed by them find application as polymerisation catalysts (V.A.Kargin, S.L.Davydova).

Uspekhi Khimii exhibits two main approaches to publishing matter on catalysis—firstly towards a deeper insight into the mechanism of several traditional catalytic processes, and secondly to acquaint the reader with new types of catalysis arising during recent years in borderline and related sciences.

Together with the classic problems of acid–base catalysis (a special form of which is difunctional catalysis—L.M.Litvinenko) the journal gives detailed consideration to all aspects of traditional heterogeneous catalysis (kinetics, thermodynamics, problems of adsorption and chemisorption). The current scientific trend in this field is to use quantum-chemical calculations and physical methods of investigation—electron spectroscopy (V.B.Kazanskii), Mössbauer spectroscopy (V.I.Gol'danskii), ferromagnetic resonance (A.A.Slinkin), internal reflectance spectroscopy, paramagnetic probes, and isotope methods (G.K.Boreskov)—to study the surfaces of catalysts and to determine the nature of the intermediate surface compounds formed. The interest long taken by the journal in the catalytic hydrogenation of carbon monoxide to the hydrocarbons of synthetic liquid fuel (the Fischer–Tropsch reaction) has also been freshly stimulated by progress in understanding that this process involves intermediate formation of carbonyl and carbonyl–hydride complexes of transition metals.

During recent years the discovery of fundamentally new types of compounds to serve as heterogeneous catalysts (e.g. lamellar compounds of graphite—M.E.Vol'pin, Yu.N.Novikov) has been accompanied by the development of homogeneous metal-complex catalysis, which plays an important part in exploiting new opportunities for the industrial organic synthesis of several most important products—monomers for polymerisation and polycondensation, alcohols, aldehydes, ketones, carboxylic acids and esters, amines, alkyl halides—from a comparatively accessible unsaturated starting material (alkenes and alkynes). Reviews in the journal suggest that homogeneous catalysis is now a borderline discipline, whose theoretical basis comprises recent advances in organometallic, organic, coordination, and quantum chemistry and which has applications to chemical industry and technology. Theoretical research in this field is currently directed at establishing the nature of the catalytically active centres in stereospecific coordination and coordination–ionic polymerisation (B.A.Dolgoplosk) and studying the detailed mechanism of the catalytic reactions of organic compounds. In some approaches (M.L.Khidekel') coordination of reactive unsaturated ligands with coordinatively unsaturated metal atoms may be a factor removing orbital prohibitions on subsequent chemical reactions by concerted mechanisms.

The journal covers also new types of catalysis—hetero-homogeneous combining the ideas of heterogeneous and homogeneous catalysis, micellar due to special factors at the interface between colloidal micelles and the external medium, and finally phase-transfer catalysis in which the transport of active reactant species to the interface is effected by additions of special surface-active agents (M.Mankosha).

In organometallic chemistry, which now plays a key role in the development of related sciences, the journal publishes matter surveying the results of many years of systematic research and opens up new prospects for organometallic synthesis and the investigation of reaction mechanisms. It comprises reviews on the discovery of carbene complexes of transition metals (E.O.Fisher), the preparation of new types of organometallic compounds, analogues of alkenes and ketones having a multiple bond linking a carbon atom with a Group IV metal (L.E.Gusel'nikov, V.M.Vdovin, N.S.Nametkin), a review by the authors of the Taylor–McKillop reaction, which has enabled thallium(I) compounds to be introduced into the everyday practice of organic synthesis, and finally papers on the preparation and properties of silatranes (M.G.Voronkov) and polymetallic chains (M.G.Bochkarev). Consideration has been given also to organometallic peroxy-compounds (G.A.Razuvaev) and their rearrangements, dinuclear complexes of transition metals containing nitrogen bridging ligands (M.I.Rybinskaya, L.V.Rybin), oxidation of organometallic compounds by transition-metal salts (I.P.Beletskaya, A.N.Kashin), possibilities of using carbonyl chloride in the chemistry of functionally substituted silicon

derivatives (V.F.Mironov, V.D.Sheludyakov), preparation and properties of ethynyl derivatives of Group IV elements, and the chemistry and practical applications of silver and copper acetylides (A.M.Sladkov).

Recent advances in the chemistry of organophosphorus compounds are illustrated by new derivatives of quinquevalent phosphorus (G.Wittig), compounds containing phosphorus–phosphorus (I.F.Lutsenko, M.V.Proskurnina) and phosphorus–hydrogen (E.E.Nifant'ev) bonds, and optically active thiophosphates. Ever new physical phenomena are now being discovered for organophosphorus compounds—e.g. diastereoisomeric intermolecular interactions, studied in detail by nuclear magnetic resonance (M.I.Kabachnik et al.), synthetic possibilities such as the capacity for involvement in 1,3-cycloaddition (A.N.Pudovik), and also new practical applications as insecticides (N.N.Mel'nikov) and, in the case of alkylenediphosphine dioxides, as complexones (M.I.Kabachnik).

Uspekhi Khimii has widely illumined during recent years the introduction into modern hetero-organic chemistry of physical methods of investigation—thermochemistry, nuclear magnetic and quadrupole resonance, infrared spectroscopy (N.A.Chumaevskii), the vibrational spectroscopy of hydrogen-bonded and charge-transfer complexes, and polarography (S.P.Gubin, L.I.Denisovich)—which in several cases have provided new structural information on organometallic compounds and have broadened current views on their reactivity. Among theoretical concepts that have evolved in hetero-organic chemistry during the 1960–1970s are the important role of solvation and intramolecular coordination (O.Yu.Oxlobystin, A.K.Prokof'ev), the organometallic α-effect (M.G.Voronkov, V.P.Feshin), the nature of the siloxane bond (M.G.Voronkov, Yu.A.Yuzhelevskii), the role of non-bonding electron-pairs of the phosphorus atom in organophosphorus chemistry (M.I.Kabachnik, E.N.Tsvetkov), and the use of $\alpha\pi$- and $d_\pi p_\pi$-conjugation effects to explain the properties of carbon–metal and heteroelement–metal bonds. On the fairly controversial topic of the role of *d*-orbitals in hetero-organic chemistry (H.Jaffé published his review in 1957) the journal has even published several articles in which it has provided a forum for both supporters (A.N.Egorochkin) and critics (N.P.Gambaryan, L.M.Epshtein, D.A.Bochvar) of this concept.

A new interest of the journal during recent years has been work on hetero-organic medicinals—biological activity of silicon compounds (M.G.Voronkov, E.Ya.Lukevits), antitumour action of certain platinum complexes—and also on industrially convenient methods of obtaining organometallic compounds from atomic metals in the gas phase (G.A.Domrachev) and their practical application to the production of films, coatings (G.A.Domrachev, O.N.Suvorova) and ultrapure substances (B.G.Gribov).

In 1967 *Uspekhi Khimii* published an article by N.S.Zefirov on "Soviet Organic Chemistry after Fifty Years" (containing more than 600 references). Since that period elapsed many new and interesting advances have been made in this field, several evident on the pages of the journal. Although contributions on this subject have generally been exhaustive in character, with a considerable breadth of coverage of both experimental and theoretical work, a few overlapping fields have been treated in depth, and in the review activity of the journal on organic chemistry five main trends can now be distinguished, giving in total a very complete view of the current state of this scientific discipline.

Firstly, systematic publication is continuing of reviews on general aspects of the chemistry of a number of important classes or organic compounds, including thi-irans (A.V.Fokin, A.F.Kolomiets), carbon suboxide, small carbon rings (E.Vogel), tropylium and cyclopropenylium cations, organic peroxides (V.Karnozhitskii), triptycenes (V.R.Skvarchenko), sterically hindered phenols and cyclohexadienones (V.V.Ershov, G.A.Nikiforov, A.A.Volod'kin), and cyclododeca-1,5,9-triene (L.I.Zakharkin). The chemistry of saturated and unsaturated functionally substituted open-chain and cyclic systems containing oxygen, sulphur, and especially nitrogen atoms in various states of oxidation is also undergoing development. Such systems exhibit considerable chemical activity and offer various structural opportunities for organic synthesis, as the journal has shown for pernitriles (N.S.Zefirov, D.I.Makhon'kov), tetracyanoquinodimethane (B.P.Bespalov, V.V.Titov), chloro-derivatives of nitriles (E.M.Movsum-zade), hydrazones (Yu.P.Kitaev, B.I.Buzykin), nitro- and diazo-derivatives, nitramines and nitrosamines (S.S.Novikov, A.L.Fridman, S.L.Ioffe, V.A.Tartakovskii), as well as systems containing a nitrogen–nitrogen bond (B.V.Gidaspov) and *N*-fluoroimines (A.V.Fokin).

A definite tradition of the journal has been to pay special attention to the chemistry of heterocycles, which has always been represented very broadly, with detailed examination of three–seven-membered systems containing one or more heteroatoms, including aromatic derivatives and their benzoanalogues. Together with oxygen heterocycles—2-pyrones, enolic δ-lactones (R.Ya.Levina, N.P.Shusherina, E.A.Luk'yanets), 1,3-dioxans, $\Delta^{\alpha\beta}$-butenolides, pyrylium salts—and the still fairly exotic derivatives of selenium (2,1,3-thia- and selena-diazoles—V.G.Lesin), tellurium (tellurans—V.I.Minkin), and phosphorus (1,3,2-dihetero-phospholans and -phosphorinans—R.A.Cherkasov, M.A.Pudovik, A.N.Pudovik; E.E.Nifant'ev—and oxaphosphorinans—B.A.Arbuzov), the bulk of the material relates to nitrogen heterocycles—benzoisoquinolines, azafluorenes, indolizines, γ-piperidones (N.S.Prostakov), azaindoles, quinuclidines (L.N.Yakhontov), perimidines (A.F.Pozharskii), indoles and indolines (M.N.Preobrazhenskaya), aziridines (A.P.Sineokov, V.S.Etlis), 1,4-benzodiazepines (A.V.Bogatskii), quinolizidines, indolizidines, pyrrolizidines (I.M.Skvortsov), purines, oxapurines (E.S.Golovchinskaya), pyridine bases (M.Ya.Karpeiskii), sydnones (V.G.Yashunskii), quinolinium salts (B.M.Gutsulyak), *N*-acylated pyridines (A.K.Sheinkman, S.I.Suminov, A.N.Kost)—and many other compounds. In all these papers detailed consideration is given to methods of preparation of the systems, their structure (an important part in whose determination is played by various physical methods) and reactivity, and also many practical applications (in particular as analytical reagents—V.M.Ivanov). Reviews by R.A.Khmel'nitskii, P.B.Terent'ev, and N.S.Vul'fson, V.G.Zankin (coumarins, quinolizidine alkaloids) have discussed the mass-spectral behaviour of heterocycles. The journal pays close attention also to the theoretical problems of heterocyclic chemistry—prototropic tautomerism (A.R.Katritzky), application of the principle of hard and soft acids and bases to the coordination chemistry of azoles (V.N.Sheinker, A.D.Garnovskii, O.A.Osipov), mechanisms of recyclisation (O.P.Shvaika, V.N.Artemov), of condensation with elimination of ammonia (B.A.Geller), and of electrophilic substitution in 3-hydroxypyridines (K.M.Dyumaev, L.D.Smirnov) and other heterocycles and arenes (L.D.Smirnov) and other heterocycles and arenes (L.I.Belen'kii), and also the Fischer reaction and its analogues (I.I.Grandberg).

The special value of many classes of organic compounds (including some containing heterocyclic structural fragments) is largely due to their natural origin or their role in metabolic processes (including genetic aspects). The steady attention paid by the journal to structural and synthetic aspects of the chemistry of natural products and bio-organic chemistry is now responsible for a major independent line

in its work. Thus during recent years it has covered questions of the structure, biosynthesis, and properties of several important biopolymers of animal origin—chitin (E.A.Plisko, S.N.Danilov)—and vegetable origin—e.g. cellulose, its biologically active derivatives, and dextrans (A.D.Virnik), lignin (O.P.Grushnikov)—and also progress in and problems of solid-phase peptide synthesis (Yu.P.Shvachkin), the chemistry of glycero- and inosito-phosphatides and myoinositol (V.I.Shvets, B.A.Klyashitskii), phosphamides, laws of the three-dimensional structure of nucleosides, nucleotides, and oligonucleotides (N.N.Preobrazhenskaya, Z.A.Shabarova), and chemical methods of synthesis of their amino-acid and peptide derivatives (B.P.Gottikh). The journal continues actively to inform readers also on current directions in the search for natural and synthetic medicinals, which in several cases is able to reveal quantitative relations between chemical structure and biological activity (S.V.Nizhnii, N.E.Epshtein). Thus special reviews have been devoted to aminoglycosidic antibiotics, antimycotics, and glycosamidines, analogues of vitamin D_3, derivatives of γ-aminobutyric acid, as well as heterocyclic analogues of prostaglandins and steroids (A.A.Akhrem, Yu.A.Titov and G.N.Dorofeenko, G.I.Zhungietu), barbiturates (E.A.Cherkasova), anaesthetics (S.V.Bogatkov), chemical searchlight radar (V.G.Yashunskii), and bis-2-chloroethyl derivatives of amino-acids and peptides possessing antitumour activity (L.P.Rasteikene, M.I.Dagene, I.L.Knunyants).

The third trend in the output of the journal on organic chemistry is the provision of information on recent research on reactions involving organic compounds. Reactions or rearrangements having the most general significance are selected for review, many of which have become during recent years independent synthetic methods. Such are ionic hydrogenation and catalytic ionic hydrogenation (D.N.Kursanov, Z.N.Parnes), 1,5-sigmatropic migration in dienyl systems (V.A.Mironov, A.A.Akhrem), degenerate rearrangements of *O*-metallated *o*-semiquinolate radicals (M.I.Kabachnik, A.I.Prokof'ev), heterocyclisations involving acetylene (B.A.Trofimov), acyl migrations in unsaturated compounds (V.I.Minkin, L.P.Olekhnovich, Yu.A.Zhdanov), and also β-ketovinylation (M.I.Rybinskaya, A.N.Nesmeyanov, N.K.Kochetkov), aromatic nucleophilic substitution (O.N.Chupakhin), dimerisation of alkenes (V.Sh.Fel'dblyum), the Wurtz reaction, oxidative decarboxylation of carboxylic acids, and oxidation of alkylaromatic compounds (I.P.Beletskaya, D.I.Makhon'kov, Yu.A.Serguchev).

The fourth, vast area of reviews on organic chemistry, concerned with the mechanism of organic reactions, is represented by matter on the kinetics and the stereochemistry of such important processes as cleavage of the epoxide ring, hydroxymercuration, substitution, elimination, and incorporation. As before, *Uspekhi Khimii* is paying close and systematic attention to all the advances in research on the various kinds of unstable intermediate species that can be found in organic reactions. The number of such species has increased considerably in comparison with earlier periods of the journal. For example, perfluorinated carbanions and arenonium ions, dehydroarenes (arynes) arising from *o*-halogenated organometallic aryl systems (O.M.Nefedov, A.I.D'yachenko, A.K.Prokof'ev), and carbenes, in particular, which may be formed by α-elimination (G.Köbrich), have become very important. Long ago the journal forecast, as it were, the blossoming of this field of chemistry, publishing in 1934 its first review on the carbene theme (containing, incidentally, only eight references to the literature).

Apart from the classic carbocations (carbonium and carbenium ions) appearing in electrophilic reactions (G.Olah) and the free radicals generated in various homolytic processes, importance is now attached to radical-ion species (O.Yu.Okhlobystin, A.S.Morkovnik), of interest with respect to stereochemical features (Z.V.Todres). Material in the journal shows that cationic and anionic radical species can be formed in chemical reactions both in consequence of one-electron transfer as the primary step in the chemical process (K.A.Bilevich, O.Yu.Okhlobystin) and in a special type of hetero-homolytic mechanism such as radical–nucleophilic substitution (I.P.Beletskaya, V.N.Drozd). It is fundamentally significant that many of these modern radical-ion processes often take place by chain mechanisms, the importance of which in chemistry was realised in the very first years of *Uspekhi Khimii* and which it has covered in detail at all later stages. The chemistry of homolytic species is in general the longest established theme in the journal. Since the times of A.E.Arbuzov, who published his review on the chemistry of organic free radicals as early as the first volume, the structural variety and the range of thermodynamic and kinetic stability of these species have greatly expanded—from stable radicals (including nitroxyl, phenoxyl, and organometallic) to extremely unstable reactive intermediates capable of taking part in new molecular rearrangements (R.Kh.Freidlina, A.B.Terent'ev, G.I.Nikitin, A.D.Stepukhovich).

Ion-pairs constitute another type of intermediate to which the journal has paid close attention, especially during recent years. They have an important role, firstly in practice, since their formation enables the true mechanism of several reactions to be understood and the latter to be controlled (e.g. the anodic polymerisation of alkenes—M.Szwarc); and secondly in general theoretical terms, for it has emerged that taking into account the intermediate formation of ion-pair species is important for a fuller understanding of the state both of classic carbocations and of carbanions in solution. According to modern theoretical ideas discussed in the journal, ion-pairs play an important part in the mechanism of electrophilic and nucleophilic substitution at a saturated carbon atom (I.P.Beletskaya, A.A.Solov'yanov).

Finally, the fifth direction in which the journal covers organic chemistry is the development of modern theoretical principles and concepts of physical organic chemistry, on which are now based both planned organic synthesis and the study of mechanisms of chemical processes involving organic compounds. Such coverage includes theoretical aspects of the equilibrium acidity of carbon–hydrogen bonds (O.A.Reutov, I.P.Beletskaya, K.P.Butin), progress concerning the nature of the dual reactivity of ambident ions (O.A.Reutov, A.L.Kurts), the nature of differences in the acidity of organic and hetero-organic compounds on passing from condensed to gas phases (M.I.Kabachnik), role of hydrogen bonding in nucleophilic substitution, prototropy of triad nitrogen-containing systems, metallotropy, and transmission and nature of substituent effects in organic and hetero-organic molecules (D.N.Krasvtsov). Modern theoretical organic chemistry appears in the journal as such a varied scientific field that it finds room even for fertile qualitative concepts of intuitive character, such as e.g. the well known ideas on strained double bonds (L.I.Belen'kii, V.I.Sokolov, N.S.Zefirov), used successfully to explain peculiarities in the oxidation of strained cycloalkenes (V.V.Voronenkov) and for strictly quantitative approaches based on an orbital (L.Salem) or a kinetic–thermodynamic analysis of the theory of chemical reactivity (R.Zahradnik) and, as already mentioned, the principles of selectivity in chemical processes (N.M.Emanuel'). Further development of this area of investigation may arise also from advances in quantum-chemical calculations on complicated molecules, covered in reviews by C.Coulson, V.G.Dashevskii (conformational energies of organic compounds), A.A.Ovchinnikov, I.A.Misurkin (conjugated π-electron systems).

As before, *Uspekhi Khimii* has actively covered during recent years new physical methods for the investigation of organic and inorganic compounds, striving to keep the reader informed about the latest advances—infrared photochemistry (Yu.A.Molin), resonance Raman effect (P.P.Shorygin), mass spectrometry with chemical ionisation (O.S.Chizhov), dynamic nuclear magnetic resonance (N.M.Sergeev), and X-ray structural analysis—the last of which has created a revolutionary situation in crystallography (W.C.Hamilton). The n.m.r. method now permits the study of heterophase solvation (G.S.Bystrov), and the electron spin resonance method for investigating complicated molecular systems containing special spin labels has found several important applications in chemistry and biology. Useful tabular and reference data with exhaustive analyses have been given in reviews on the thermochemistry of organometallic compounds (I.B.Rabinovich) and the search for molecules possessing enhanced electron affinity (L.N.Sidorov). Among physicochemical matter special mention must be made of several contributions especially useful with respect to experimental method—reviews by E.N.Gur'yanova on "Mathematical Treatment of Results of Physicochemical Research on Complex Compounds" and by A.N.Korol' on "Reproducibility of Retention and Identification Data in Gas–Liquid Chromatography", as well as a few early journal papers that are still of interest—International System of Retention Factors in Gas Chromatography (for results obtained by this method see review by R.V.Golovnya), "Nomographic Methods in Physical Chemistry", and "Errors in and Accuracy of Measurements" (1947).

In concluding this survey we shall examine the character of the most recent material on the chemistry of macromolecular compounds, which at the present time, perhaps, is absorbing in the highest measure all the latest advances both in related fundamental scientific disciplines and in the instrumental technique of modern scientific research. The journal reflects all the chief lines of development, among which a few main trends in scientific research can be noted.

Firstly, new systems are constantly used in the formation of polymers, the main tendency being that, apart from purely organic monomers—acetylenes and diynes, dialkenylaromatic (B.A.Krentsel') and alkyl systems, adamantane derivatives, and mono- and bis-α-diketones (E.S.Krongauz)—enhanced importance is being attached to macromolecular derivatives of the most diverse elements—nitrogen (polyimides based on nitrogen heterocycles, polycyclotrimerisation of aromatic nitriles and acetylenes (V.A.Sergeev, V.K.Shitikov, V.A.Pankratov), polyisocyanates (S.G.Entelis), polytriazines, polyazaporphyrins (A.A.Berlin) and polyquinoxamines, and also thermostable polymers from tetramines and aromatic tetracarboxylic dianhydrides), fluorine (fluorination of polyethers and polythioethers, polyfluorovinyl), sulphur (polymers based on alkene sulphides and αβ-unsaturated sulphur-containing compounds—E.N.Prilezbaeva), phosphorus (and also polyphosphazens and oligomers of organo-oxaphosphazens—E.F.Chernyshev), and silicon (including organosiloxazans and oligodialkylsiloxanes—V.V.Korshak, A.A.Zhdanov). Broad investigations have been made also on polymers based on carboranes (V.V.Korshak) and ferrocene, various inorganic and metal-containing macromolecules (V.A.Kargin), and also coordination polymers.

Secondly, an intense search is being made for ever new promoters, initiators, and catalysts of the formation of macromolecular compounds, and detailed investigation of their mechanism is being based on the latest advances in physical organic, organometallic, coordination, and quantum chemistry. Methods are being elaborated for the polymerisation of chemically activated monomers, and redox reactions are acquiring great value in polymerisation processes—e.g. initiation by one-electron oxidation or reduction (including electrochemical) with formation of active intermediate radical-ions (N.G.Gaylord) or oxidative polymerisation of vinyl monomers and reductive polyheterocyclisation—a new method of synthesis of polyheteroarylenes. In several cases initiating systems based on readily oxidisable organic derivatives of non-transition metals (E.B.Milovskaya) cause radical polymerisation of polar monomers; derivatives of magnesium (B.L.Erusalimskii) and alkaline-earth metals (A.A.Arest-Yakubovich) initiate anionic polymerisation. The main laws governing the capacity of lactams for anionic polymerisation as a function of their structure are being established, and new activators for this process investigated (T.M.Frunze, V.V.Kurashev). Study continues of the mechanism of, and the nature of active centres for, stereospecific polymerisation of alkenes under conditions of metal-complex catalysis by transition metals (B.A.Dolgoplosk), while linking the ideas of anionic and coordination forms of catalysis has led to the discovery of anionic–coordination polymerisation (S.S.Medvedev). Finally, detailed research on the mechanism of polymerisation continues by the application of quantum-chemical and spectroscopic methods: the kinetics (and in the case of emulsion polymerisation also the topochemistry) of individual stages and the influence of the solvent are being studied, rates of growth and termination measured, and quantitative theories formulated to explain polycondensation processes and also (with the application of topological principles—S.Ya.Frenkel') random and heterophase copolymerisation.

Advances in the synthetic chemistry of macromolecular compounds (the title of a recent review by V.V.Korshak) involve at the present time the formation of many classes of polymeric molecules, which is apparently the third major line of development. Only in recent years have syntheses been accomplished of block copolymers of polycondensation type (P.M.Valetskii), semi-rigid chain molecules, ladder polyheteroarylenes (A.L.Rusanov), skeleton and network polymers (Ya.S.Vygodskii, S.V.Vinogradova—interpenetrating networks), polymers having a stellar or comb-like structure, ion-exchange membranes (B.N.Laskorin), oligo- and polyphenylenes with functional groups, and finally poly(arylene sulphides) (V.A.Sergeev, V.K.Shitikov, Ya.N.Nedel'kin).

The most diverse synthetic methods, several using novel types of catalysts (including stereospecific for optically active polymers—E.L.Klabunovskii), are now employed to obtain the bulk of such varied classes of compounds. Since many of these methods often acquire independent scientific and practical value, their exploitation represents a fourth line of research in polymer chemistry during recent years. This has been closely followed in the journal by the inclusion of reviews on polycondensation methods, of value for the synthesis of thermostable polymers, which have been covered also by special reviews (V.V.Korshak, S.V.Vinogradova, A.A.Berlin), on copolymerisation of cyclic compounds (T.M.Frunze, V.V.Kurashev), and on hydro-dehydropolymerisation and isomerisation polymerisation of unsaturated hydrocarbons (B.A.Krentsel'). Detailed discussions have appeared also on non-equilibrium copolycondensation in homogeneous systems, solid-phase polymerisation(V.E.Shklover, Yu.T.Struchkov), and heterophase radical polymerisation, as well as on polycyclisation, polycyclotrimerisation, trimerisation polycondensation (M.M.Teplyakov), and acceptor–catalytic polyesterification (V.A.Vasnev).

Many of the macromolecular compounds obtained during these years possess most interesting properties of practical value, such as the ability to catalyse chemical reactions and stabilise polymers (N.A.Plate) and to form macromolecular

charge-transfer complexes. Several of these polymers show great technical promise—e.g. electrical, photoelectric, and photochromic—as well as photoconduction and electrophotographic phenomena in linear polymers containing saturated and conjugated bonds. Semiconducting pyropolymers, conjugated inorganic polymers based on carbon (M.I.Cherkashin), and vitreous carbon (M.Ya.Fioshin) have also been obtained. Progress in the structural study of polymeric carbon has been surveyed by A.M.Sladkov.

Many of these properties are also of great theoretical interest (thus a quantum-chemical interpretation of the electronic structure and properties of polymers containing conjugated bonds has been given in a paper by A.A.Ovchinnikov, I.A.Misurkin), while others are of interest in biochemistry (use of polymers as matrices for peptide synthesis, formation of biologically active cellulose derivatives, use of polyethylene glycol in biochemistry, the grafting of biologically active compounds to the surface of optical materials, and the preparation of polymeric biological chemotherapeutic agents having carcinolytic activity), as well as for other purposes (e.g. use of ion-exchange resins in photometry, development of thermostable antifriction plastics (I.A.Gribova, S.V.Vinogradova), and formation of coatings by anodic electrodeposition of water-thinned paint systems based on water-soluble oligomers).

In view of the extraordinary value of polymeric substances for the most varied branches of practical science and technology, all this work probably indicates yet another, fifth line of research in modern polymer chemistry—the synthesis of macromolecular substances and materials having specified properties—for which those properties that are directly related to the service characteristics of macromolecular compounds are, naturally, of especial interest. In this connection the journal has continually published during recent years matter on the mechanism of stabilisation and the thermal stability of polymers and its dependence on their chemical structure (V.V.Korshak, S.V.Vinogradova), including cation- and anion-exchange resins, frost-resistance of polymers, their plasticisation, improving the water resistance of fibreglass plastics by additions of water-repellent adhesives, and finally problems of the photodegradation (M.B.Neiman), photostabilisation, and photostability of polymers (including coloured materials).

Finally, the sixth trend in macromolecular chemistry now evident in the journal is the physical chemistry and the physicochemical mechanics of polymer substances and materials, whose development also is regarded as very important. General contributions on this subject cover a wide range of problems—molecular-mass distribution in the production of homopolymers (N.S.Enikolopov), chemical defects in heterounit polymer molecules (V.V.Korshak), composition inhomogeneity of polymers (S.Ya.Frenkel'), and finally the nature of supermolecular structures in rubbers (V.A.Kargin). Great attention has been paid to the structure and properties of heat-resistant polymers (A.A.Askadskii, G.L.Slonimskii), block polymers and their solutions (L.Z.Rogovina, G.L.Slonimskii), and amorphous polymers, as well as to mechanisms of the diffusion of electrolytes (G.E.Zaikov) and the sorption of certain polymers in relation to their porous structure.

The most diverse physical methods are now used in solving physicochemical problems of macromolecular chemistry—sedimentation of polydisperse polymers, n.m.r. study of systems comprising a polymer with a substance of low molecular mass, electrochromism (for the study of slow movements in macromolecules), and also study of surface electrical characteristics of polymer-containing disperse systems—low-temperature methods being covered in a special review by A.G.Merzhanov). In combination with progress in developing new approaches to a theoretical interpretation of the experimental results this work has yielded in recent years very important quantitative data for several individual polymers, their mixtures, and solutions. Examples are studies of ion exchange and the swelling of exchangers, of structural features of homo- and co-polyurethanes and of networks based on heat-resistant polymers, of dilatancy of colloid structures and polymer solutions, of conformational and thermodynamic properties of macromolecules in ternary polymer systems, and of the polymeric structure of selenium also photoelectric phenomena. Furthermore, the influence of hydrogen bonding and ionic interactions has been established on several carboxyl-containing copolymers and ionomers based on them, and also that of a solid surface on relaxation and structure formation in polymer boundary layers (a theory of the "isofree" volume and the glass transition was constructed for amorphous polymers).

The value of such research is that the results can be used in the exploitation of macromolecular substances and materials. This applies in particular to investigations on the nature of gel formation, the structure and properties of polymer gels, also changes in rheological properties accompanying the formation and transformation of polymers, and those of thermosetting resins. Furthermore, the importance of modern research on the physics of polymers, to which the journal has recently paid such close attention, lies in the theoretical possibility of using the resulting quantitative characteristics to predict important practical properties of new synthetic macromolecular compounds. A recent review was devoted to methods for calculating physical parameters of high polymers (A.A.Askadskii, G.L.Slonimskii).

A survey of the contents of *Uspekhi Khimii* in the modern period must take note of two additional tendencies. The first is a definite increase in the number of contributions in which purely scientific interest in a research field is combined with great applied significance. Examples are a detailed examination of the ozonolysis of alkenes (an important method for obtaining dibasic carboxylic acids and other carbonyl compounds—G.A.Tolstikov), a long-term comprehensive study of radical reactions of 1,3-dioxans—an important class of saturated heterocycles—which are extremely promising compounds in organic synthesis (D.L.Rakhmankulov, S.S.Zlotskii, R.A.Karakhanov, U.B.Imashev, V.V.Zorin), and finally an analysis of current prospects for the use of organosulphur compounds present in crude petroleum and the determination of trace elements (Yu.A.Zolotov).

A second clear trend is for the journal to establish new headings. Examples are provided by new interrelations found between chemical and biological kinetics (N.M.Emanuel'), enabling the quantitative laws of many most complicated biological processes to be investigated and the effectiveness of several medicinal (including antitumour) preparations to be assessed and optimum régimes determined, the regular appearance of matter on synthetic food products—"Ways of using Amino-acids in Industry", "Plasteins in Nutrition", and "Chemistry of Odour and Flavour" (V.M.Belikov, S.V.Rogozhin, B.V.Tolstoguzov, R.V.Golovnya)—the discovery of new chemical possibilities in recording and storing information (A.V.Vannikov), including the use of photosensitive enzyme systems (I.V.Berezin, K.Martinek), papers on problems of silverfree photography, high-temperature exciton conduction, and photocatalytic conversion of solar energy (K.I.Zamaraev), and papers on enzyme electrodes. The contents have covered also aspects of the prebiological evolution of organic substances, and quite recently ecological questions, at present causing great interest throughout the world in connection with global problems of the protection of the environment. The great work of the journal is now actively crystallising the views of wide circles of its readers and

guiding them in the saturation flow of world chemical information has required that it should make its own appraisals of the relevance of reviews in various fields of chemical science.

Activity in scientific information during recent years was summarised at a 1977 All-Union conference on "Problems in the Improvement of Review Information on Chemistry", at which the chief editor of *Uspekhi Khimii*, Academician N.M.Emanuel', gave a lecture on "Criteria of the Quality of Reviews in the Field of Chemistry"†. He showed that, since it is chemical science that now produces the greatest amount of experimental material (especially on organic chemistry), while being actively involved in forming new fields of science and creating interdisciplinary networks, chemical literature has constituted during recent years an especially weighty portion of the total flow of world scientific and technical information#. Since for ordinary chemical journals (not only original but also abstracts) it is now difficult to ensure effective identification of scientific papers and facilitate their retrieval, the most efficient route for disseminating information, incorporating it, and bringing it to the attention of chemists is the review literature, with its inherent ability to condense primary scientific information, as well as its critical analysis and skilled generalisation.

The journal now considers that an immediate task, as was mentioned later, is to examine the possibility of condensing primary information by publishing analytical surveys. Numerical data in several leading science and science-assessing papers have shown that such analytical review activity enhances considerably the efficiency of scientific work and in several cases may lead to economies in the material resources consumed in scientific research.

To assess the quality of review literature the lecture proposed the use of a special "condensation factor", equal to the ratio of the volume of the primary information to that of the scientific review and representing the saving in the time of the specialist reader. A yearly analysis in the lecture showed that for *Uspekhi Khimii* the factor has more than doubled (its value at ten-year intervals from 1936 to 1976 was 20, 26, 36, 50, and 50), and has now apparently reached an optimum value (in the opinion of specialists further increase would heighten the risk of distorting the primary scientific information).

Later in the lecture it was stated that the most objective quantitative criterion of the scientific value of review papers may be their citation index, which depends exponentially on two factors—topicality, i.e. timeliness of a particular item, and timeless scientific importance—and as a rule (although these are exceptions) diminishes with the time that has elapsed since publication. According to statistics given in the lecture the number of highly quoted papers (>4–5 references in 3 years) in *Uspekhi Khimii* for the period 1961–1969 was ~7% of the total number of publications, more than double the index for ordinary (non-review) academic scientific journals on chemistry.

In the concluding part of the lecture it was shown that reviews published in *Uspekhi Khimii* are usually cited regularly by all the major journals published in various countries. For all years the maximum numbers of citations are found in the *Journal of the American Chemical Society* (1240 references), *Journal of Organic Chemistry* (360), and *Journal of Chemical Physics* (310). Each of the other major science journals examined contains on the average 240 citations, which over all the journals amounts to >12000 references to items in *Uspekhi Khimii* (of which >1000 in 1972)[7]§.

All these statistics confirm that our leading review journal fulfills successfully its scientific information function, and is up to the standard of modern demands on world analytical review literature.

The journal has also played an important scientific educational role in the training of science personnel. Throughout its many years *Uspekhi Khimii*, whose editorial board has contained at various times many most eminent representatives of chemical science, has educated its active expert staff and writers. Matter published in it has enabled many scientific workers to improve thei qualifications and prepare to solve complicated scientific problems, and workers in applied fields of chemistry, engineers, and works laboratory technicians to find on its pages valuable practical tips for everyday work. Reviews in the journal have always been widely used to raise the level of instruction in chemistry and chemical technology in higher education, and its contents have always been useful to students for their undergraduate and degree work. It is now difficult to imagine modern candidate or doctoral theses, monographs, handbooks, or textbooks without references to *Uspekhi Khimii*.

The geographical range of the journal's activity is constantly expanding. Among its authors have been chemists in Moscow and Leningrad, Riga, Vilnius and Tallinn, Kiev and Minsk, Kharkov, Donetsk, Rostov-on-Don, Ufa and Kazan, Gorky and Sverdlovsk, Irkutsk and Novosibirsk, Erevan, Baku, Tashkent and Dushanbe—i.e. all those towns in which new science and information centres have grown and developed, and important and interesting results have been obtained in various modern fields of chemistry. The journal regularly contains also contributions from leading research workers in the USA, Japan, the Federal Republic of Germany, France, England, Czechoslovakia, Poland, Bulgaria, Italy, Switzerland, and many other countries.

Results obtained from a questionnaire on improving review information in the country recently issued to our chemical community¶ are objective and significant for a general appraisal of the work of the journal. Many of the specialists questioned (10000 questionnaires were distributed among workers in academic and specialised scientific organisations, as well as higher educational institutions) named *Uspekhi Khimii* as their principal source of general chemical information, and expressed satisfaction with its work.

We can be confident that *Uspekhi Khimii* will continue to fulfill its important function of review journal, shedding light on prospects of development for current chemical trends.

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†The conference was held in Moscow on the initiative of the Moscow administration of the Mendeleev All-Union Chemical Society, the editorial board of the society's journal, the local organisation of the Nesmeyanov Institute of Heteroorganic Compounds of the USSR Academy of Sciences, and the Chemistry Section of the Moscow Scientists Club. A précis of the lecture was published[6].

#Estimates by several experts indicate that its proportion increased between 1968 and 1976 from 18.7% to 23% of the total number of published items.

§The citation index of *Uspekhi Khimii* rose sharply in the 1960s, from the first issue of a complete ("cover-to-cover") English translation (published under the title Russian Chemical Reviews from January 1960 by the Royal Society of Chemistry, Burlington House, London, in collaboration with the British Library).

¶The enquiry was conducted in 1981 by the Section on Review Information on Chemistry and Chemical Technology of the Central Administration of the Mendeleev All-Union Chemical Society together with the Chemistry Division of the All-Union Institute of Scientific and Technical Information of the USSR Academy of Sciences.

All readers heartily congratulate their journal on its fine jubilee and wish it further achievements in its efficient contribution to the progress of world chemical science.

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Activation of Oxygen by Cytochrome P-450 and Other Haemoproteins

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Data on the activation of molecular oxygen by the full microsomal hydroxylating system containing cytochrome P-450 as the terminal oxygenase are examined*. The nature of the hydroxylating agent, which is the oxenoid $Fe^{3+}O$, is analysed. The autoxidation reactions of cytochrome P-450 from various sources, haemoglobin, myoglobin, and peroxidases are compared and the role of the axial ligands of the haem iron and the structure of the active centres of the haemoproteins in this process is demonstrated. The possible mechanisms of the oxidation of organic compounds by peroxides with participation of cytochrome P-450, cytochrome *c*, haemoglobin, and catalase are examined critically. Haemoproteins have been divided into three groups in terms of the type of peroxide oxidation reactions. The relative contributions of the radical and two-electron reactions in the oxidation of compounds by peroxides with participation of different haemoproteins are analysed.
The bibliography includes 184 references.

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I. INTRODUCTION

Hydroxylating enzyme systems which employ molecular oxygen as the oxidant and require pyridine nucleotides (NADH or NADPH) for their functioning are widely distributed in the living world. The large number of reactions catalysed by such systems are characterised by the following stoichiometry:

$$AH + NADPH(NADH) + H^+ + O_2 \rightarrow AOH + NADP^+(NAD^+) + H_2O.$$

The enzymes which insert one oxygen atom in the substrate and reduce another oxygen atom to water are called monoxygenases or mixed-function oxidases[1-18]. The most numerous group of monoxygenases consists of involved multienzyme complexes containing unique haemoproteins as the terminal oxidase—cytochromes P-450. Hydroxylating systems of this type are present in human and animal liver microsomes and adrenal cortex mitochondria and form part of the composition of the cells of many bacteria, yeasts, and fungi, are constituents of the liver cells of cold-blooded animals, and are present in certain higher plants.

The liver microsomal hydroxylating system has attracted particular attention in connection with the great importance of its functions. This system oxidises endogenic substrates (steroids and cholesterol) and numerous xenobiotics entering the organism, including drugs, poisons, carcinogens, industrial chemicals from the environment, etc. The liver microsomal hydroxylating system consists of three components, each of which has been fully characterised[7,11,17,18]: NADPH–cytochrome P-450 reductase (EC 1.6.2.4), cytochromes P-450 (EC 1.14.14.1), the existence of many forms of which has been convincingly demonstrated[11], and phospholipids[9]. The steroid hydroxylating system from adrenal cortex mitochondria also consists of three components: adrenodoxin reductase (EC 1.6.7.1), ferredoxin (adrenodoxin), and two forms of cytochrome P-450, one of which is responsible for the reactions involving the scission of the cholesterol side chain ($P\text{-}450_{scc}$) and the other is responsible for the 11-β-hydroxylation reaction of steroids ($P\text{-}450_{11\beta}$).[18] The camphor-hydroxylation bacterial system also includes three components: putidaredoxin reductase, ferredoxin (putidaredoxin), and cytochrome $P\text{-}450_{cam}$.[18,19] As a result of the efforts of investigators from many countries, the most significant aspects of the structure, functions, and mechanism of the action of enzymatic hydroxylating complexes have been extensively investigated and surveyed in a series of monographs, reviews, and collections[1-19]. However, two most important problems have not been finally solved, namely the mechanism of the activation of molecular oxygen by cytochrome P-450 and the organisation of multienzyme complexes in the membranes of the endoplasmic reticulum, the adrenal cortex mitochondria, and bacterial cells.

The aim of the present review is a critical consideration and survey of the experimental data on the activation of molecular oxygen by cytochrome P-450 obtained very recently for the microsomal hydroxylating system of the liver. The ability of cytochrome P-450 to oxidise many substrates of different chemical types in combination with organic peroxides and other oxidants is extremely significant for the understanding of the mechanism of the activation of oxygen by cytochrome P-450. In this connection much attention has been devoted to reactions involving the oxidation of a substrate by hydroperoxides and other oxidants with participation of cytochrome P-450. The mechanism of the action of cytochrome P-450 differs from that of the other haemoproteins capable of catalysing many oxidative processes. One of the aims of this review is the consideration and analysis of the causes of this difference between cytochrome P-450 and other haemoproteins in oxidation-reduction processes. In order to solve the latter problem, the author has confined himself to the range of haemoproteins listed in Table 1, in view of the availability of data permitting a comparison of the reactions involving these haemoproteins and also the possibility of analysing the role of axial ligands and the structure of apoproteins in the activation of oxygen. Much attention has been devoted to the nature of the hydroxylating agents and

† The following abbreviations are used in the review: $P\text{-}450\text{-}LM_2$ = cytochrome from liver microsomes of rabbits administered phenobarbital-sodium; $P\text{-}450\text{-}LM_4$ = cytochrome from liver microsomes of rabbits administered 3-methylcholanthrene or β-naphthoflavone; $P\text{-}450_{cam}$ = cytochrome P-450 from camphor-hydroxylating bacteria; $P\text{-}450_{scc}$ = cytochrome from adrenal cortex mitochondria catalysing the scission of the cholesterol side chain; CHP = cumenyl hydroperoxide: TBHP = t-butyl hydroperoxide; DMA = *N*,*N*-dimethylaniline; ROOH = organic hydroperoxides and peracids; AH = substrate; AOH = reaction product.

Table 1. Certain characteristics of haemoproteins.

Haemoprotein	Molecular mass	Axual ligand		Absorption bands, nm			Natural source	References
		L_5	L_6	oxidised	reduced	complex with CO		
Cytochrome P-450: LM_2	48 700	S (Cys)	H_2O or N(His)	418, 535, 568	413, 544	450, 552	rabbit liver	[11, 13]
LM_4	55 300	S (Cys)		396, 645	411, 545	448, 550	rabbit liver	[11, 13]
P-450$_{cam}$	45 000	S (Cys)	N(His)	417, 535, 571	411, 540	447, 550		[19]
P-450$_{scc}$	48 000	S (Cys)	N(His)	394, 540, 565	416, 548	448, 550	mitochondria	[25]
P-450$_{11\beta}$	45 000	S (Cys)	N(His)	394, 510, 645	416, 548	448, 550	bovine adrenal cortex	[25]
Cytochrome b_5	11 000	N(His)	N(His)	413	424, 526, 556	none	calf liver	[5]
Cytochrome c	13 000	N(His-18)	S(Met-80)	407	415, 521, 550	none	horse heart	[26]
Peroxidase (EC 1.11.1.7)	40 000	N(His)	H_2O	420, 541	432, 535, 565	—	horseradish	[27, 28]
Myoglobin	17 000	N(His)	H_2O or HO^-		435, 555	423, 541, 578	sperm whale heart	[29]
Haemoglobin	68 000	N(His-82α, 92β)	H_2O or HO^-	407, 504, 538, 630	~430, ~555, ~590	419, 539, 569	human and horse blood	[29, 30]
Catalase (EC 1.11.1.6)	232 400	N(His)	HO^- or H_2O	—	—	—	ox liver, horse liver	[28, 31]

the relative contributions of the homolytic and heterolytic stages in oxidation processes with participation of the haemoproteins enumerated.

II. ACTIVATION OF MOLECULAR OXYGEN BY THE FULL MICROSOMAL HYDROXYLATING SYSTEM

We shall employ the concept of the full microsomal hydroxlating system to designate the reconstructed systems containing NADPH-cytochrome P-450 reductase, cytochrome P-450, NADPH, oxygen, and the substrate, and also in the description of the oxidation by liver microsomes with participation of NADPH and oxygen in contrast to the oxidation of substrates by hydroperoxides with participation of microsomes or individual forms of cytochrome P-450.

The process involving oxidation by microsomes and reconstructed systems is complex and consists of at least eight stages (Fig.1). In the first stage the substrate forms a complex with the oxidised form of cytochrome P-450, which is accompanied by a change in the oxidation-reduction potential and the spin state of the haemoprotein: the majority of substrates convert the low-spin form of cytochrome P-450 into the high-spin form, while certain amines induce the reverse transition. It has been suggested that the high-spin form of cytochrome P-450 loses the axial ligand in the sixth position but retains the cysteinyl group as the fifth ligand[20]. The rates of formation of the enzyme–substrate complexes are high and are characterised by constants in the range 10^2–10^6 litre mol^{-1} s^{-1} depending on the nature of the substrate[21]. The binding of substrates to cytochrome P-450 facilitates the reduction of the enzyme–substrate complex by the first electron arriving from the NADPH-specific electron transport chain[18,22]. The chain incorporates NADPH-cytochrome P-450 reductase (FP_1) and possibly cytochrome b_5. NADPH-cytochrome P-450 reductase is a flavoprotein (FP_1) with a molecular weight of approximately 79 000 and containing one FAD group and one FMN group in the molecule[23,24]. FMN reductases receive two electrons from NADPH, while FAD is involved in the transfer of these electrons to cytochrome P-450.[24] The mechanism of the action of the reductase has not been ultimately elucidated, since the relative positions of the two flavin fragments in the enzyme molecule are unknown. The second stage of the process in microsomes and in reconstructed systems consists of two phases[12]. A possible cause of the two phases in the reduction of the enzyme–substrate complex by the first electron in microsomes may be the heterogeneity of cytochrome P-450 [12,17] and, what is more likely, the different rates of reduction of different spin forms of cytochrome P-450,[32] since high-spin haemoproteins are reduced faster than the low-spin haemoproteins[20].

In the third stage the enzyme substrate complex reduced by the first electron combines rapidly with molecular oxygen: the rate constants for the addition of O_2 to different complexes vary in the range 10^4–10^6 litre mol^{-1} s^{-1}.[21] The oxygenated form of reduced cytochrome P-450 from liver microsomes was first detected spectrophotometrically in 1971 by Estabrook et al.[22] At the same time Gunsalus et al.[33] and Ishimura et al.[34] demonstrated spectroscopically the formation of a complex of oxygen with the reduced camphor-hydroxylating cytochrome P-450$_{cam}$. The camphor–P-450$_{cam}$–O_2 and P-450$_{cam}$–O_2 complexes were isolated for the first time in 1976 [35,36] by chromatography at temperatures below 0 °C in mixed aqueous organic solvents. These complexes have been characterised spectroscopically and kinetically. The camphor–P-450$_{cam}$–O_2 ternary complex undergoes autoxidation: the activation energy for this process is 18 kcal mol^{-1} in water and 19 kcal mol^{-1} in an aqueous organic medium[35].

The oxygenated complex of cytochrome P-450 was isolated for the first time in 1979 from rabbit liver microsomes at −30 °C in aqueous glycerol solution[37]. The complex is characterised by absorption maxima at 420 and 557 nm and the activation energy for [its] autoxidation is ~10 kcal mol^{-1}.[37] The ternary complex of cytochrome P-450$_{scc}$ from bovine adrenal cortex mitochrondria with cholesterol and oxygen was purified quite recently in the same medium: the complex has an absorption maximum at 414 nm and an extinction coefficient of 84 ± 2 litre mmol^{-1} cm^{-1},[38]

The complex formation reaction of highly purified cytochrome P-450 from rabbit liver microsomes (P-450-LM) has been investigated spectrophotometrically using stopped flow methods[39]. The reaction was carried out in two stages in the presence of the substrate (benzphetamine) and was found to consist of two stages: the short-lived oxygenated Complex A, having absorption maxima in the difference spectrum at 430 and 450 nm, is formed initially and is then converted into

Complex B with an absorption maximum at 440 nm. The complex formation reaction between oxygen and the reduced cytochrome is described by the scheme

$$P\text{-}450^{r}_{LM} + O_2 \xrightarrow{k_1} A \xrightarrow{k_2} B \xrightarrow{k_3} P\text{-}450^{o}_{LM}\ .$$

The rate constants are $k_1 > 6.0 \times 10^4$ min^{-1}, $k_2 = 270$ min^{-1}, and $k_3 = 3.0$ min^{-1}.[39] Complex B has spectroscopic characteristics close to those of Complex I in the reactions of peroxidases with hydrogen peroxide[28] and is probably analogous to it. The reaction components have the following Soret bands: P-450r—424 nm, P-450o—418 nm, A—432 nm, and B—421 nm. The oxidation of cytochrome P-450 in the ternary complex is the rate-limiting stage of the process and leads to the hydroxylation of the substrate.

The structure of the oxygenated haemoprotein is of primary importance for the mechanism of the activation of oxygen by cytochrome P-450. The state of oxygen in the substrate—P-450—O_2 complex and its configuration are still unknown. By analogy with oxyhaemoglobin, it has been suggested that oxygen receives an electron from the haem iron and its state is best reproduced by the structure proposed for oxyhaemoglobin by Weiss[40]: $Fe^{3+}O_2^-$ (Fig.1). By analogy with oxyhaemoglobin, one can postulate that the oxygen in the oxygenated cytochrome P-450 has the configuration Fe—O=O, in which the Fe—O=O angle is close to 120°. Attempts have been made to calculate the most favourable configuration for the oxygenated cytochrome P-450 by quantum-mechanical methods[41,42]. The calculations showed that the unusual spectroscopic properties of the oxygen and carbonyl complexes of cytochrome P-450 are fully associated with the thiol ligand in the fifth axial position and depend very strongly on the distance between the haem iron atom and the sulphur atom of the thiol ligand. An increase of this distance by 0.2 Å and more is quite sufficient to convert cytochrome P-450 into the inactive form P-420, which differs from the former by the maximum of the Soret band of the carbonyl complex of the cytochrome in the reduced state[42]. It would be premature and risky to reach definite conclusions about the configuration of oxygen in the oxygenated cytochrome P-450 on the basis of quantum-mechanical calculations, since theoretical calculations for the Fe—O_2 bond in oxyhaemoglobin proved unconvincing. Such calculations, carried out by the molecular orbital method[43], give preference to Pauling's structure[44], whereas it follows from calculations by the MO-LCAO method carried out by other workers[45] that only the closed Griffith structure[46] ensures the existence of the stable low-spin complex of oxyhaemoglobin. An X-ray diffraction study of oxygenated myoglobin confirmed Pauling's model, i.e. the axis of the O_2 molecule forms an angle close to 120° with the plane of the porphyrin ring[47].

The substrate—P-450—O_2 ternary complex in microsomal hydroxylating system is unstable and undergoes autoxidation. The reduction of this complex by yet another electron, which occurs in the fourth stage of the process (Fig.1), is necessary for the hydroxylation of the substrate. It has been suggested that the second electron comes from the NADH-specific microsomal chain containing NADH-cytochrome b_5 reductase and cytochrome b_5. Hitherto this stage of the process has not been resolved into individual steps and its rates have not been measured for microsomal systems. The important role of cytochrome b_5 in the transport of the second electron has been confirmed in the study of oxidation by microsomes[48–53] and in the oxidation of a series of substrates in reconstructed systems[54–65]. It is believed that cytochrome b_5, reduced in the NADH-specific electron transport chain, can transmit the second electron directly to cytochrome P-450.[48] The participation of cytochrome b_5 in the transport of the second electron to the ternary complex is indicated by a whole series of experimental data, which have been discussed[66].

Firstly, in the microsomal oxidation of substrates of the first type (hydrocarbons, tertiary amines, and alicyclic compounds) with participation of two pyridine-nucleotides (NADH and NADPH), a synergistic effect is observed, reflecting the important role of the two electron transport chains in the oxidation process[48,50]. The synergistic effect is not observed for substrates of the second type (aniline and other amines)[17]. It is important to note that only endogenic cytochrome b_5 participates in the synergistic effect, while the exogenic cytochrome b_5 (incorporated in the microsomal membranes) does not always stimulate microsomal oxidation and actually retards the reactions of aminopyrine and DMA.[49,66] Evidently the cytochrome b_5 incorporated in the membrane differs from the native cytochrome b_5 by the fact that it cannot enter a cluster containing cytochrome P-450 and reductase and cannot participate in the reduction of cytochrome P-450. The inhibiting effect of the cytochrome b_5 incorporated in microsomes can be explained by its ability to receive electrons from NADPH-cytochrome P-450 reductase and to consume the latter non-productively from the standpoint of the hydroxylation process. The reduction of cytochrome b_5 by NADPH-cytochrome P-450 reductase was initially merely postulated[48,50] but now it has been confirmed experimentally[17,56,59]. The different effects of the endogenic and exogenic cytochrome b_5 on the microsomal oxidation can be explained by the different oxidation-reduction potentials of the native haemoprotein and the haemoprotein incorporated in the membrane.

Secondly, in the oxidation by microsomes or reconstructed systems cytochrome b_5 frequently accelerates the oxidation of some substrates, but is indifferent in the reactions of others; the oxidation of benzo[*a*]pyrene,[53,57] acetanilide[57], 4-ipomeanol[52], benzphetamine[54], 7-ethoxycoumarin[53,55,61], and *p*-nitroanisole[59–61] is accelerated by cytochrome b_5, while the oxidation of aminopyrine[49] and aniline[66] is inhibited by this haemoprotein. It may be that the substrates of the first group form complexes with cytochrome P-450 whose oxidation-reduction potentials favour the reduction of the substrate—P-450—O_2 complexes by cytochrome b_5; on the other hand, aniline and aminopyrine form complexes with oxidation-reduction characteristics which prevent their reduction by cytochrome b_5.[49,66]

Thirdly, the influence of cytochrome b_5 on oxidation in the reconstructed systems is determined to a large extent by the nature of the cytochrome P-450 itself. Cytochrome P-450 with an increased affinity for cytochrome b_5 has been isolated recently[60] and it has been shown that the oxidation demethylation of *p*-nitroanisoles is in this case effectively accelerated by cytochrome b_5.[56,59] Cytochrome b_5 accelerates the oxidation of the same substrate, namely benzo[*a*]pyrene with different efficiencies under identical conditions in the presence of two different forms of cytochrome from rabbit liver (P-450-LM and P-450-LM_4), i.e. the nature of cytochrome P-450 determines to a significant extent the stimulating possibilities of cytochrome b_5.[62] Direct evidence has been obtained recently for the reduction of oxygenated cytochrome P-450 from liver microsomes by cytochrome b_5:[65] it was shown that the autoxidation of the oxygenated cytochrome P-450 is accelerated in the presence of reduced cytochrome b_5.

Thus the influence of cytochrome b_5 on the oxidation reactions of various substrates in microsomes and in reconstructed systems is determined by several factors: the nature of cytochrome b_5 (exogenic or endogenic) and its oxidation-reduction potential, the nature of the substrate oxidised and its influence on the oxidation-reduction characteristics

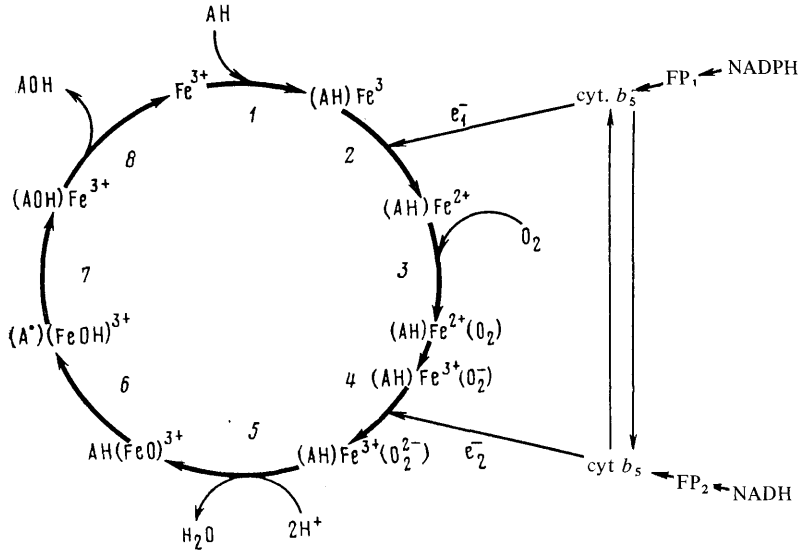


Figure 1.

of the ternary substrate–P-450–O_2 complex, and finally the nature of cytochrome P-450 itself and its affinity for cytochrome b_5. We may also note the influence of the methods used to reconstruct the enzyme systems, the content of admixtures of detergents which have not been removed, and the reaction conditions. For a favourable ratio of the oxidation-reduction parameters of cytochrome b_5 and the ternary complex, the haemoprotein stimulates the oxidation of substrates, while under the conditions of an unfavourable ratio of the above parameters, cytochrome b_5 can receive electrons from NADPH-cytochrome P-450 reductase but is incapable of transmitting them to cytochrome P-450, which retards the oxidation process.

The fourth stage of the microsomal oxidation is a complex process in which several macromolecular biocomponents of the microsomal system can participate. The rates of this stage have not so far been measured. We may note that the stage in which the ternary camphor–P-450_{cam}–O_2 complex is reduced by the second electron in the camphor-hydroxylating system has been studied in detail and characterised by its rate constants. This process proceeds with participation of an effector—putidaredoxin, and is the rate-limiting stage in the oxidation of camphor in a bacterial system[19,67].

After the reduction of the ternary complex by the second electron, the fourth stage of the process involves the hydroxylation of the substrate, the liberation of the molecules of water and the reaction product, and the regeneration of the initial catalyst in the oxidised form (Fig.1). It must be emphasised that at the present time none of these processes has been investigated separately and furthermore it is not known in what sequence the processes occur. One cannot rule out the possibility that the number of stages after the fourth may be greater or less than the four stages indicated in Fig.1. It is possible that after the fourth stage the hydroxylation step is followed by the simultaneous liberation of the molecules of the reaction product and water from the ternary complex, i.e. the complex hydroxylation step constitutes a cooperative process, which is frequently encountered in enzymatic reactions. Another possibility has been considered by White and Coon[12]: the fourth stage is followed by the cleavage of the O–O bond in the ternary complex with formation of water, the hydroxylating agent ruptures the C–H bond in the substrate, and this is followed by the formation of the reaction product, which is released in the last stage of the process. The oxidising agent has not been identified directly in any of the hydroxylating enzyme systems. Its nature and properties must be inferred from indirect data concerning the stereoselectivity and specificity of the microsomal oxidation, the presence or absence of isotope effects in the oxidation of labelled substrates and, what is very important, the similarities and differences in the oxidation of the same substrates in the complete system and with participation of hydroperoxides in combination with cytochrome P-450. The inhibition of the reactions by antioxidants, which retard the radical oxidation processes, plays an important role in the consideration of the relative contributions of the homolytic and heterolytic stages in the microsomal oxidation process[68,69]. Stages *5–8* of the process (Fig.1) will be henceforth discussed taking into account all the data concerning different aspects of the microsomal oxidation of substrates.

It is believed[12] that the fourth stage of the process is followed by the cleavage of the O–O bond in the ternary complex with formation of a hydroxylating species containing only one oxygen atom. This claim is supported by the high oxidising capacity of iodosobenzene $C_6H_5I{=}O$ and its derivatives in combination with the oxidised cytochrome P-450, first observed by Ullrich and coworkers[70]. Indeed iodosobenzene can transmit to the oxidising agent only one oxygen atom, since it has no other. Two groups of investigators were able to obtain with the aid of iodosobenzene relatively stable compounds simulating the hydroxylating agent of cytochrome P-450, which contains only one oxygen atom[71,72]: the oxidation of hydrocarbons by iodosobenzene is catalysed by chlorodimethylferriprotoporphyrin IX,[71] while in the presence of octaethylporphyrinatoiron(III) chloride in $CHCl_3$ or CH_2Cl_2 2-iodoso-*m*-xylene gives rise to a species whose magnetic susceptibility corresponds to the high-spin state of iron(IV).[72] It is believed[72] that the structure of the compound obtained is analogous to that of Complex I of

peroxidases, catalases, and chloroperoxidase and is characterised by the following formulae:

$$P^{+}Fe^{IV}O^{2-} \longleftrightarrow PFe^{IV}O^{-} \longleftrightarrow PFe^{III}O \ ,$$

where P is the porphyrin. The high degree of oxidation of iron in these model complexes is stabilised, according to the authors, by the porphyrin ring, which gives up one electron to the iron or oxygen atom. In many instances evidence has been obtained for the existence of porphyrin cations[73,74]. The species whose structure is illustrated above is called oxene[18,75], since its oxygen atom contains six electrons in the outer shell and is distinguished by a high reactivity, by analogy with carbenes and nitrenes[76,77]. As a result of the cleavage of the O–O bond in the ternary complex, such a species is in fact formed in the scheme proposed by White and Coon[12]. The O–O bond dissociation process takes place with participation of the carboxy-group of one of the aminoacids of the active centre of cytochrome P-450 (Fig.2). The authors believe that the structure of the peracid formed on interaction of the carboxy-group of the oxygen complex of cytochrome P-450 is favourable for the subsequent cleavage of the O–O bond and the formation of the hydroxylating species. This consideration is confirmed by the high hydroxylating capacity of peracids in relation to aromatic and aliphatic hydrocarbons, which increases when the peracids are coordinated to metal complexes. It is not fortuitous that peracids are convenient models of monoxygenases simulating the step in which oxygen is inserted in the substrates of the microsomol system[4,75,78]. It is believed[12] that the oxenoid formed in stage 5 (Fig.1) is stabilised by the thiol ligand of cytochrome P-450, which constitutes an unusual reservoir of electrons in the formation of the hydroxylating species and its reactions:

$$S^{-}Fe^{V}O^{2-} \longleftrightarrow S^{-}Fe^{IV}O^{-} \longleftrightarrow S^{-}Fe^{III}O \leftrightarrow S^{\cdot}Fe^{III}O^{-} \ .$$

The possibility of the involvement of the carboxy-group of one of the aminoacids of the active centre of cytochrome P-450 in the formation of the hydroxylating agent has been confirmed experimentally[79] in relation to cytochrome P-450$_{cam}$.

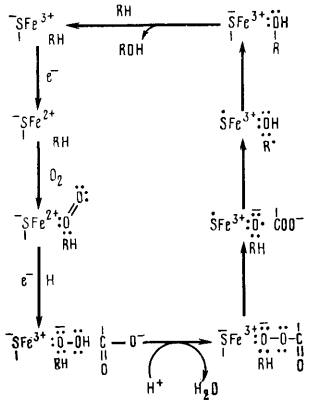
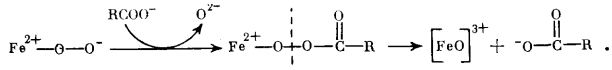


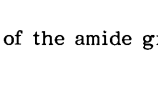
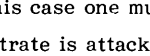
Figure 2.

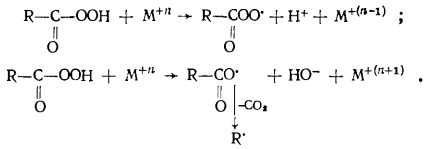
Using labelled oxygen ($^{18}O_2$), it has been shown[79] that dihydrolipoic acid acylates the distal oxygen atom in the oxygenated complex P-450$_{cam}$ $^{18}O_2$, forming an intermediate peroxy-compound, the dissociation of the O–O bond of which is greatly facilitated, which results in the insertion of one ^{18}O atom in camphor and of the other in the carboxylate group of dihydrolipoic acid:



The heterolytic decomposition of an acyl peroxide results in the formation of the oxenoid $[Fe^{18}O]^{3+}$ and lipoic acid labelled in the carboxy-group:



As an alternative to the heterolytic decomposition of the acyl peroxide formed as a result of the covalent binding of the carboxy-group of the aminoacid to the oxygenated cytochrome P-450, the possibility of the homolytic decomposition of the intemediate peroxy-compound, formed with participation of the amide group  , has been considered[12]. In this case one must postulate that the C–H bond in the substrate is attacked by the amidyl radical  . We believe that this reaction pathway is unlikely, because the amidyl radical is relatively stable and at temperatures close to physiological temperatures cannot rupture the stable C–H bond in the majority of substrates of cytochrome P-450. The homolytic dissociation of the O–O bond in the intermediate acyl peroxide must also be ruled out, because the homolysis of this bond with participation of metal complexes and ions is accompanied by the decarboxylation of the acylperoxy-radical formed[80]:

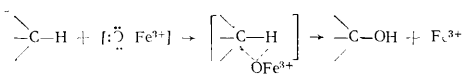


As a result of the last reaction, the acid of the apoenzyme participating in the covalent fixation of oxygen in the oxygenated cytochrome P-450 would be irreversibly consumed and the catalyst would rapidly break down.

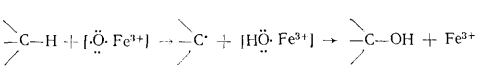
Thus the most probable pathway leading to the formation of the oxenoid in the complete microsomal system is heterolytic decomposition of the acyl peroxide formed on interaction of the carboxy-group of one of the aminoacids of the active centre with the activated oxygen of the ternary substrate–P-450–O_2 complex reduced by the second electron. It is important to note that the oxygen coordinated to cytochrome P-450 is not only fixed to the matrix of the enzyme, as suggested for oxyhaemoglobin[44,81], but is covalently bound to one of the acids of the apoenzyme with formation of an intermediate peroxy-compound.

In the sixth stage of the process (Fig.1) a C–H bond in the substrate molecule is ruptured. It is believed[12] that this stage proceeds via a radical mechanism. This claim is supported by experimental data, which we shall consider in detail below. The electronic structure and reactivity of the oxenoid $[Fe^{3+}O \leftrightarrow Fe^{4+}O^{-}]$ are completely unknown. Presumably one of two mechanisms of attack on the substrate

obtains[16,18]: the first (oxenoid) or two-electron mechanism:



and the second (cryptoradical) or one-electron mechanism:



It would be incorrect to claim that one of the reaction pathways is universal. If the oxygen in the oxenoid is in the singlet state, the first mechanism operates, in which the oxygen atom is inserted in the C–H bond without its dissociation, as happens in the reactions of carbenes, nitrenes, and atomic oxygen with aromatic and aliphatic hydrocarbons[76,77,78]. This reaction pathway is most likely in oxidation reactions of aromatic compounds and is the only one possible in the microsomal oxidation of cyclohexene and other unsaturated compounds and it is difficult to imagine the formation of epoxy-derivatives of cyclohexene and olefins via a radical mechanism. If the oxenoid is in the triplet state, then the direct insertion of the oyxgen atom in the substrate is impossible—such a reaction is spin-prohibited. In this case the one-electron, cryptoradical mechanism operates, which is reflected in the scheme (Figs.1 and 2). The radical mechanism of the oxidation reaction in the complete microsomal system has been supported by a number of pieces of important evidence.

Table 2. The primary isotope effects (k_H/k_D) in the microsomal oxidation of various substrates.

Substrate	k_H/k_D	References
[CD_3]Morphine	1.4	83
[α-D_2]Ethylbenzene	1.8	84
[D_{12}]Cyclohexane	1.0	85
[11-D_2]Lauric acid	3.0	86
[9-D_2]Caproic acid	3.0	86
Saturated compounds	1.4	87
[16α-D]Pregnenolone	3.0	88
[7α-^{3}H]Taurodeoxycholic acid	3.8	89
[α-D_2]Isopropylamphetamine	1.6	90
[CD_3]-*o*-Nitroanisole	2.0	91
[Cd_3]Methoxyanisole	10.0	92
Aromatic compounds	1.3-1.75	93
[1,1-D_2]-1,3-Diphenylpropane	11.0	94
Biphenyl	1.4	95
N,N'-Dimethylphentermine	1.4	96
Norbornane	11.5	97
7-Ethoxycoumarin	13.5	98

Firstly, a mixture of methylcyclohexanols with the isomer ratios 1° : 2° : 3° = 0.072 : 1 : 1.25 has been obtained in the hydroxylation of methylcyclohexene with participation of cytochrome P-450-LM_2.[82] Such proportions of the reaction products are consistent with a radical process mechanism.

Secondly, the dissociation of the C–H bond in the microsomal oxidation process is supported by the primary isotope effects, which have been observed in a number of instances (Table 2). It is remarkable that, in the oxidation of aromatic compounds of the benzene series and biphenyl, the isotope effects are small: k_H/k_D = 1.3–1.8. Small isotope effects have also been obtained for the oxidative dealkylation reactions of [CD_3] morphine[83], *N,N'*-dimethylphentermine[96], [CD_3]-*o*-anisole, and [α-D_2]isopropylamphetamine[90,91]. This means that the oxidation of aromatic compounds and oxidative dealkylation of certain substances either do not involve the dissociation of the C–H bonds or this process is not rate-limiting. In a number of instances measurements have been made of the intramolecular isotope effect which occurs when the molecule contains hydrogen and deuterium in the same position. The microsomal oxidation of *exo, exo, exo, exo*-tetradeuteronorborane yielded a mixture of *endo*- and *exo*-2-norborneols[97]. The ratio of the *exo*- and *endo*-alcohols was 3.4 : 1 for norbornane, decreasing to 0.76 : 1 for the deuterated substrate. The isotope effect was 11.5 in this instance[97]. It was shown in the same study that the oxidation of norbornane is not accompanied by the complete retention of configuration on formation of the alcohol, which confirms the intermediate formation of the carbon-containing radical. Measurements have been made recently of the isotope effect in the *O*-de-ethylation of 7-ethoxycoumarin[98] in the oxidation by two cytochromes from rat liver microsomes—P-450 and P-448. The ratios k_H/k_D were 11.8 and 13.5 for P-450 and P-448 respectively. The large isotope effects in a number of instances confirm that the rate-limiting stage of the microsomal oxidation process involves the dissociation of the C–H bonds in the substrates.

Thirdly, systematic kinetic studies of the influence of 1-naphthol and mannitol on the oxidation of aniline and DMA by microsomes with participation of NADPH and O_2 and by reconstructed systems with participation of the same cofactors demonstrated an effective retarding effect of 1-naphthol[69]. The 1-naphthol concentrations were significantly lower than those of both substrates and the mixed type of inhibition in the oxidation of the two substrates cannot therefore be accounted for solely by their competition with the inhibitor for binding to cytochrome P-450. Under the experimental conditions, 1-naphthol serves as an effective trap for active radicals participating in the oxidation reaction, whereas mannitol does not retard the oxidation process. The results led to the conclusion that radicals may participate in the oxidation of aniline and DMA in the complete microsomal system[69].

Thus the proportions of the reaction products in the oxidation of hydrocarbons, the large primary isotope effects in the oxidation of a series of substrates, the inhibiting effect of antioxidants on the oxidation of aniline and DMA, and the partial retention of configuration in the oxidation of norbornane confirm the possibility of radical stages in oxidation by the complete microsomal system.

The last stage of the microsomal oxidation reaction (Fig.1) is associated with the liberation of the reaction product from the ternary complex and the regeneration of cytochrome P-450 in the initial stage. This stage is rapid, since the more polar reaction products are less strongly bound to cytochrome P-450 than the less polar substrates and are easily displaced by the substrate molecules from the active centre of the enzyme.

The problem of the determination of the rate-limiting stage of the microsomal oxidation reaction is fairly complex. We may note immediately that the rate-limiting stages in the oxidation of the same substrate in microsomes and reconstructed systems may differ.

Extensive kinetic data concerning the oxidation of various substances by microsomes and the rates of invdividual stages of the process were considered previously[16,18]. Here the reader should merely be reminded that some of the stages of the microsomal oxidation reactions are known beforehand to

be incapable of being rate-limiting. The interaction of many substrates with oxidised cytochrome P-450 takes place at high rates[18,21] and the reduction of the enzyme–substrate complex by NADPH-cytochrome P-450 reductase is also rapid and it has been shown[21,99] that it cannot limit the rate of the entire oxidation process. The third reaction stage, namely the binding of molecular oxygen to the reduced enzyme–substrate complex, has high rate constants in the range 10^3–10^6 litre $mol^{-1}s^{-1}$.[21] It has so far been impossible to estimate the rate of reduction of the ternary complex by the second electron in the fourth stage of the microsomal oxidation process. It is sometimes suggested that this stage can in fact limit the rate of the process as a whole[12,17]. An analogy is frequently drawn between the microsomal system and the bacterial camphor-oxidising hydroxylating system in which the stage involving the reduction of the ternary camphor–P-450_{cam}–O_2 complex by the second electron is the rate-limiting stage for the process as a whole[19,67]. However, this analogy may be erroneous, because the reduction of the ternary complex by the second electron in the bacterial system involves yet another protein—putidaredoxin. On the other hand, the turnover number in the microsomal system is less than one-tenth of that in the hydroxylation of camphor with participation of P-450_{cam}.[12]

The most correct solution of the problem of the nature of the rate-limiting stage in the microsomal oxidation process involves the measurement of the rates of all the stages of the complex process and their comparison. Such a study has been carried out in Sato's laboratory in connection with the oxidation of benzphetamine in a reconstructed system[99]. Table 3 presents the kinetic characteristics of the individual stages of the process.

Table 3. The kinetic parameters k and ν of the N-demethylation of benzphetamine in the reconstructed systems of liver microsomes[99].

Stage of the process	Kinetic characteristics
Binding of benzphetamine to cytochrome P-450	$k_1 = 50\ s^{-1}$
Reduction of enzyme-substrate complex by first electron	$k_2 = 4\text{–}12\ s^{-1}$
Binding of oxygen to enzyme-substrate complex	$k_3 = (1.0\text{–}1.3) \times 10^3\ s^{-1}$
Decomposition of ternary complex with formation of reaction products	$\nu \geqslant 2.3$
Oxidation of NADPH	$\nu = 0.8\text{–}1.2$
Accumulation of formaldehyde	$\nu = 0.5\text{–}0.7$

Note. The rates of the processes are given in nmol s^{-1} per nmol of cytochrome P-450.

Analysis of the rates of the individual stages of the oxidation of benzphetamine led the authors[99] to the conclusion that the rate-limiting stage may be either the reduction of the ternary complex by the second electron or any process after this step, since the reaction product accumulates at rates less than the rate of decomposition of the ternary complex.

Some years ago we suggested that the rate-limiting stage of the microsomal oxidation process is the attack on the substrate in the ternary complex by the hydroxylating agent accompanied by the dissociation of the attacked C–H bond[100,101]. This hypothesis is supported by several experimental facts. Firstly, as already mentioned, large primary isotope effects are observed in the microsomal oxidation in most cases (Table 2), which implies the dissociation of the C–H bonds in the substrate molecule in the rate-limiting stage of the reaction. If such dissociation occurred before or after the rate-limiting stage, it would be impossible to obtain isotope effects of 11–13.

Secondly, there exist the so-called uncoupling compounds which are bound effectively to cytochrome P-450 but are not oxidised by microsomes. They include fully fluorinated hydrocarbons[102–105]; in this case the C–F bonds are very stable and cannot be ruptured by the oxidising agent in the rate-limiting stage.

Thirdly, we have shown that, in the complete microsomal system and with participation of hydroperoxides, the kinetic and energetic characteristics of the oxidation of the same substrates are in both cases very close or do not differ at all. This may reflect the attack on the substrate by the same oxidising agent in both systems. However, in the hydroperoxide oxidation there is no necessity for the transport of two electrons to the oxidising agent, since the oxygen of the hydroperoxide is already activated by two electrons. Consequently both systems may have the same rate-limiting stage, involving the transformation of the ternary complex containing the substrate, cytochrome P-450, and oxygen in the first case and the substrate, cytochrome P-450 and the hydroperoxide in the second. This is apparently entirely valid for the majority of substrates, although one cannot ignore certain differences between the oxidation by microsomes in the complete system and the oxidation with participation of hydroperoxides. The differences between the two systems will be discussed below.

In conclusion of this section, it must be emphasised that the rate-limiting stage of the microsomal oxidation reaction can vary as a function of the reaction conditions. A change in the process temperature is extremely significant from this point of view. The microsomal phospholipids undergo phase transformations at temperatures in the range 17–20 °C, which affect the energetic characteristics of the oxidation of the same substrates: the activation energies for the oxidation of substrates of the first type above the phase transition temperatures vary in the range 9–14 kcal mol^{-1}; at temperatures below the phase transition temperature, the activation energies increase to 17–25 kcal mol^{-1}.[106] The break in the relations between the oxidation rate constants and temperature and the points corresponding to the phase transitions of the microsomal phospholipids can denote a change in the rate-limiting stage of the process: above the break point under the conditions of enhanced mobility of cytochrome P-450 and the reductase, their interaction is facilitated and does not limit the rate of oxidation; below the phase transition point, the liquid-crystal state of the membrane lipids hinders contact between the two enzymes and the stage involving the reduction of cytochrome P-450 by the reductase may limit the rate of the entire process. The activation energies below the break point may therefore refer to the stage in which cytochrome P-450 is reduced by the reductase, while the activation energies above the break point may refer to another stage, for example, the decomposition of the ternary complex with formation of the reaction product or to the dissociation of a C–H bond by the hydroxylating agent in the ternary complex.

III. AUTOXIDATION OF HAEMOPROTEINS

Comparative analysis of the autoxidation of haemoproteins is useful from two points of view: firstly, the autoxidation of myoglobin and haemoglobin constitutes the only method of

activation of molecular oxygen by these proteins and, secondly, comparison of the rates of autoxidation of haemoproteins makes it possible to estimate the role of the axial ligands and the structure of the apoenzyme in the activation of oxygen by haemoproteins. Table 4 presents certain characteristics of the oxygenated complexes of haemoproteins. It shows that the oxygenated complexes of five haemoproteins are characterised by similar absorption spectra. All the proteins enumerated undergo autoxidation. It has been shown that the oxidation of cytochromes P-450$_{cam}$ and P-450-LM$_2$ results in the formation of the superoxide radical-anions $O_2^{\cdot-}$.[108-111] Somewhat unexpectedly, the $O_2^{\cdot-}$ radical-anions could not be detected by direct methods in the autoxidation of cytochrome P-450-LM$_4$ from the liver microsomes of rabbits given β-naphthoflavone[112]. Some authors erroneously attributed to the $O_2^{\cdot-}$ radical-anion the role of the hydroxylating species in the microsomal oxidation on the grounds that the oxidation processes are inhibited by superoxide dismutase and copper complexes which can model this enzyme[113]. A detailed study of the inhibition of the oxidation of DMA by copper(II) ions and the copper(II) complexes of tyrosine and lysine showed that the role of the copper compounds reduces to the interaction with the $O_2^{\cdot-}$ radical-anion and to displacing the equilibrium to the right[114]:

$$[Fe^{2+}O_2 \equiv Fe^{3+}O_2^{\cdot-}] \rightleftarrows Fe^{3+} + O_2^{\cdot-} .$$

This process leads to the non-productive consumption of the oxygenated cytochrome P-450 and competes with the reduction of the latter by the second electron, i.e. lowers the concentration of the hydroxylating species in the system and thereby retards the oxidation. Copper compounds also enter into other reactions which, together with that discussed above, are responsible for the complex mixed type of inhibition in the oxidation of DMA by rabbit liver microsomes[114].

Table 4. Characteristics of oxygenated complexes of haemoproteins.

System	λ_{max}, nm	E^*, kcal mol^{-1}	References
S-P-450$_{cam}$-O_2	418, 552	17.0; 18.0	19, 35, 36
P-450$_{cam}$-O_2	—	24.0; 14.5	19, 35, 36
S-P-450$_{scc}$-O_2	414	—	38
P-450-LM$_2$-O_2	420, 557	9.6	37
Haemoglobin-O_2	412, 542, 577	17.7	29, 107
Myoglobin-O_2	417, 544, 582	—	29

*E = activation energy for the oxidation reaction.

Myoglobin and haemoglobin are autoxidised very slowly, which is not surprising, since their main function is to transfer molecular oxygen and not to activate it. Nevertheless it has been shown repeatedly that the oxidation of myoglobin and haemoglobin results in the formation of the radical-anions $O_2^{\cdot-}$.[81] The autoxidation of oxygen-transferring proteins has attracted the attention of investigators for a long time[115]. At the present time it is entirely possible to consider the main pathways leading to the autoxidation of myglobin and haemoglobin. There are three mechanisms of the oxidation of these proteins:

$$Fe^{2+}O_2 + H_2O \rightleftarrows Fe^{3+}OH_2 + O_2^{\cdot-} , \quad (1)$$

$$Fe^{2+}O_2 + Fe^{2+} \rightleftarrows Fe^{2+}O_2Fe^{2+} \rightarrow 2Fe^{3+} + O_2^{2-} , \quad (2)$$

$$Fe^{2+}O_2 + H \text{ (or } e^-) \rightarrow Fe^{3+}O_2H \rightarrow \text{products.} \quad (3)$$

Reaction (1) is an important stage of the autoxidation of iron-porphyrins, but the formation of $O_2^{\cdot-}$ or $HO_2^{\cdot}$ is hindered by the hydrophobic environment within the protein. Comparison of the corresponding oxidation-reduction potentials shows that the reactions of simple ions are endothermic and for this reason can hardly constitute the main pathway in the autoxidation of myoglobin and haemoglobin at pH 7:

$$Fe^{2+} + O_2 \rightarrow Fe^{3+}OH_2 + O_2^{\cdot-} ,$$
$$Fe^{2+}O_2 \rightarrow Fe^{3+}OH_2 + O_2^{\cdot-} ,$$

Reaction (1) may become the principal stage in the autoxidation of haemoglobin if the oxidation-reduction potential of the Fe^{2+}/Fe^{3+} pair is significantly reduced. Such reduction of the potential is possible when histidine in the fifth axial position is replaced by another ligand, for example, tyrosine or cysteine, which is observed in certain mutant haemoglobins. However, the axial ligand is not the only species which can decrease the oxidation-reduction potential of the haemoprotein; this can be done by the protein itself. Indeed, myoglobin, haemoglobin, and peroxidase have the same fifth axial ligand (histidine), but they have different oxidation-reduction potentials and as a consequence their oxygenated complexes have different capacities for autoxidation (Table 5). Table 5 shows that the capacity for autoxidation of oxygenated haemoproteins increases with decrease of the oxidation-reduction potential, which decreases markedly on replacement of the fifth ligand (histidine in myoglobin, haemoglobin, and peroxidases) by cysteine (in cytochromes P-450).

Table 5. The oxidation-reduction potential (E_0') of haemoproteins and qualitative comparison of the stabilities of their oxygenated complexes $Fe^{2+} + O_2$ (K).

Haemoprotein	E_0' (pH 7), V	K	References
Haemoglobin	+0.2	very stable	115
Myoglobin	+0.1	very stable	115
Turnip peroxidase, P$_7$	-0.12	stable for 20 min	115
Horseradish peroxidase	-0.25	oxidises rapidly, not detected	115
S-P-450$_{cam}$	-0.17	oxidises very rapidly	19, 35, 36
P-450$_{cam}$	-0.27	stable only at -30 °C	19, 35, 36

Reaction (2) is unlikely for protein iron-porphyrins, since the protein hinders the dimerisation of the oxygenated form by reaction with another porphyrin molecule, but such dimerisation has been observed for non-protein iron-porphyrins. It is noteworthy that the dismutation of two Fe^{2+}–P-450$_{cam}$–O_2 complex species has been demonstrated for the bacterial hydroxylating system[19]:

$$2[Fe^{3+}\text{—P-450}_{cam}\text{—}O_2^{\cdot-}] \rightarrow Fe^{3+}\text{—P-450}_{cam} + O_2^{2-} + Fe^{3+}\text{—P-450}_{cam} + O_2 .$$

This is possible only in the case of the association of two molecules of cytochrome P-450$_{cam}$, which cannot be ruled out.

The oxidation of the oxygenated myoglobin and haemoglobin usually takes place with participation of a donor of a hydrogen atom or an electron [reaction (3)]. Such donors can be nitrite[116], phenol[116], 1-naphthol[107], aniline[30], phenylhydrazine[117], and other organic and inorganic reductants. It has been shown that oxyhaemoglobin oxidises these reductants via a radical mechanism[107,118]. The activation energy for the oxidation of 1-naphthol by oxyhaemoglobin is 17.7 kcal mol^{-1}.[107]

In the absence of electron donors, oxyhaemoglobin is fairly stable and different techniques, for example, flash photolysis (λ = 300 nm), must be used to generate the O_2^- radical-anion[119].

Thus oxyhaemoglobin and oxymyoglobin are distinguished under normal conditions by a greater stability compared with other oxygenated haemoproteins. It has been suggested that this stability is ensured by the structure of the oxygen-transferring proteins and, in particular, by the important role of the distal histidine moiety, which stabilises oxygen by forming hydrogen bonds with it.[44] However, slow oxidation of myoglobin and haemoglobin nevertheless occurs and in oxygenated blood there is usually a steady-state concentration of methaemoglobin $Fe_3^{3+}OH_2$, amounting to 1–2%. In the presence of H^+ ions or electron donors, the oxidation of haemoglobin is accelerated: for example, the aniline hydroxylase activity of erythrocytes has been convincingly demonstrated. Haemoglobin, which is not usually regarded as an enzyme, catalyses the oxidation of aniline to *p*-aminophenol[120]:

$$\text{aniline} + Fe^{2+}O_2 \rightarrow \text{aniline}\cdot Fe^{2+}O_2 \xrightarrow{e^-,2H^+} p\text{-aminophenol} + Fe^{3+} + H_2O .$$

It is important to note that the oxygenated cytochromes P-450$_{cam}$ and P-450-LM$_4$ are incapable of oxidising their substrates[18,19]. In the former case the oxidation requires reduced putidaredoxin—the effector of the oxidation of camphor and in the latter case oxidation takes place in the presence of reduced cytochrome b_5.[121] This parallelism suggests that in the microsomal system cytochrome b_5 can play the role of an effector analogous to that of the Fe- and S-containing putidaredoxin in the bacterial camphor-oxidising system. In the literature there is only one indication of the oxidising capacity of oxygenated cytochrome P-450-LM$_2$ in the absence of electron donors[122]. However, we believe that these data have been obtained using a doubtful analysis of the reaction product and require additional confirmation.

In conclusion of this section, we emphasise yet again that the autoxidation of haemoproteins takes place with formation of the O_2^- radical-anion, which is not itself a hydroxylating species but on recombination can give rise to hydrogen peroxide, which is a source of the active oxidant radical-anions $HO^{\cdot}$. The rates of oxidation of haemoproteins are determined by the oxidation-reduction potentials of the Fe^{2+}/Fe^{3+} pair and increase sharply when histidine in the fifth axial position (myoglobin, haemoglobin, and peroxidases) is replaced by cysteine (cytochromes P-450). The oxidation-reduction potential of iron-porphyrins is determined not only by the nature of the fifth axial ligand but also by the structure of the protein itself. The distal histidine in the myoglobin and haemoglobin molecules probably significantly stabilises the oxy-complexes of these oxygen-transferring haemoproteins, protecting them from autoxidation with liberation of the toxic radical-anion O_2^-. The activation of oxygen in the coordination sphere of cytochrome P-450 is ensured by its anomalously low oxidation-reduction potential.

IV. THE MECHANISMS OF THE CATALYSIS OF PEROXIDE OXIDATION BY HAEMOPROTEINS

It has already been mentioned that oxidised cytochrome P-450 combined with organic hydroperoxide catalyses the oxidation of many substrates of the microsomal system. After the first study by Kadlubar et al.[123], in which the ability of liver microsomes to catalyse reactions involving the oxidative dealkylation of amines by hydroperoxides was demonstrated, numerous investigations, surveyed and discussed in a series of reviews[12,16,124], were carried out. It is known that cytochromes P-450-LM$_2$, P-450$_{cam}$, and certain others are catalytically active in peroxide oxidation[16,125]. On the other hand, it has not been possible to detect a catalytic activity of cytochrome P-450-LM$_4$ in peroxide oxidation[126,127]. The range of oxidants employed is extremely wide and includes, apart from organic hydroperoxides (CHP and TBHP), also peracids, hydrogen peroxide[128], sodium periodate[129], sodium chlorite[130], iodosobenzene[70], iodosobenzene diacetate[131], and pyridine *N*-oxide[132]. The number of reactions catalysed by cytochrome P-450 when peroxy- and non-peroxy-oxidants are used is also large: oxidation of aromatic compounds[106,133–140], oxidative *O*- and *N*-dealkylation of aromatic compounds[106,133–140], oxidative *O*- and *N*-dealkylation of ethers and tertiary amines[123,130,141–148], epoxidation of cyclohexene[100], oxidation of saturated and alicyclic compounds[149–151], and oxidation of aliphatic alcohols[152]. Thus all reactions catalysed by microsomal cytochrome P-450 in the complete system can take place in the presence of peroxides[16,18]. The peroxide oxidation of the lipids in the microsomal membranes, in which radical initiation reactions may play a significant role on interaction of lipid peroxides with membrane haemoproteins, occupies an important place. The formation of lipid peroxides has been investigated in detail[5]. Two systems for the peroxide oxidation of unsaturated aliphatic acids exist in the microsomal fraction: a non-enzymatic system in which iron is reduced by ascorbic acid and an enzymatic system in which the reductant is NADPH. The endogenic haem iron atoms serve as the inducing centres. The consideration of the important class of lipid peroxide oxidation reactions is outside the framework of this review, since it is of independent interest. We shall merely mention that the reactions of lipid peroxides with cytochrome P-450 may become an important source for the generation of the active radicals $RO^{\cdot}$ and $RO_2^{\cdot}$ via mechanisms which will be discussed in detail below. In the first stages of their investigations, several groups of workers postulated that the oxidising agent in peroxide oxidation is Complex I (Fig.3), analogous to the well known intermediate complex in the reactions of peroxidases, catalases, and chloroperoxidase[100,133–143]. The formation of Complex I in the hydroperoxide system and its comparison with the formation of the same agent in the complete microsomal system are presented in Fig.3. This analysis is supported by several important experimental data. Firstly, different spectra, identical with the spectra of Complex I for certain peroxidases (for example, cytochrome *c* peroxidases), have been recorded in the interaction of hydroperoxides with microsomes or with the highly purified cytochrome P-450-LM$_2$.[153] Table 6 presents the characteristics of the difference spectra of the complexes of hydroperoxides with cytochrome P-450 and other haemoproteins. Secondly, when microsomes were mixed with CHP, the EPR spectrum of a product having a *g*-factor of 2.0 was recorded, i.e. a radical species analogous to Complex I is formed[154]. Thirdly, the oxidation of [4-^{3}H]acetanilidine in the hydroperoxide system yielded the same NIH shifts as in the complete microsomal system, i.e. the mechanism of the insertion of an oxygen atom in acetanilide is the same in both cases[155]. Fourthly, as already mentioned, the oxidation of many substrates in the complete and hydroperoxide systems yielded similar or identical kinetic and energetic parameters for the oxidation of the same substrate in the two systems[18,100,101]. All the facts enumerated above confirm the hypothesis put forward by several workers that the mechanisms of the oxidation reactions in the complete and hydroperoxide systems are similar[16,100,146] and make it possible to postulate the existence of the same hydroxylating agent in both systems—the oxenoid [$Fe^{3+}O \leftrightarrow Fe^{4+}O^-$], analogous to Complex I of per-

oxidases and catalases. However, a series of results have been obtained recently indicating a more complex mechanism of the hydroperoxide oxidation and possible differences between the hydroxylating agent and Complex I.

Table 6. Spectroscopic characteristics of the complexes of haemoproteins with hydroperoxides.

Haemoprotein	Hydroperoxide	λ_{max}, nm	λ_{min}, nm	K_S, mmol litre^{-1}	References
Microsomes	CHP	441	422	—	154
" "	tetralinyl hydroperoxide	380, 440	420	—	160
" "	TBHP	380, 440	418	—	160
" "	CHP	380, 440	418	—	136
" "	CHP	440	418	0.043	161
Cytochrome P-450-LM_2	CHP	440	413—415	0.120	162
Cytochrome P-450-LM_2	ROOH*	436—440	418	—	128
Cytochrome *c*	CHP	433	413	0.083	163
Haemoglobin	CHP	425	405	0.100	164

*Substituted perbenzoic acids, substituted CHP, and substituted benzyl hydroperoxides were used here; K_S = dissociation constant of complex.

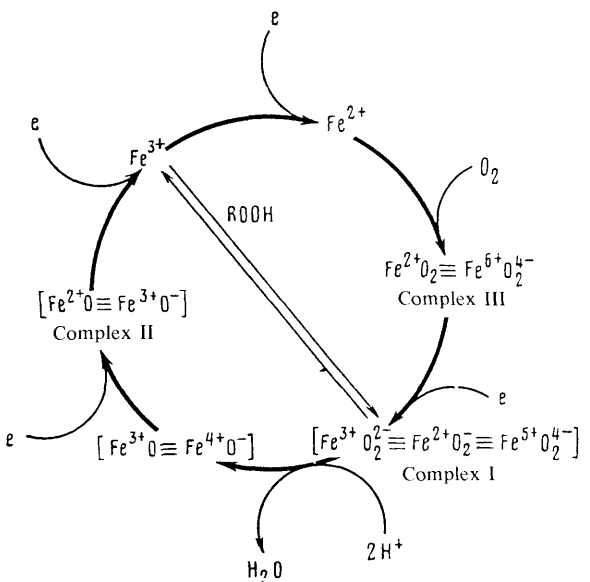
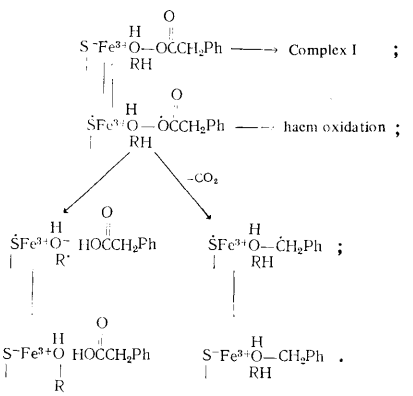


Figure 3.

The application of spectrophotometry and stopped flow techniques permitted a detailed investigation of the interaction of a large number of substituted perbenzoic acids, CHP derivatives, and benzyl hydroperoxide derivatives with cytochrome P-450-LM_2 and to reconstruct the absolute absorption spectra of the intermediate compounds formed[128]. Spectra differing appreciably for different peroxides were obtained as a result. The absolute absorption spectrum of a mixture of *m*-chloroperbenzoic acid with cytochrome P-450-LM_2 is characterised, in particular, by maxima at 375, 425, and 540 nm. This spectrum differs significantly from the known spectra of Complexes I: Complexes I of peroxidase and catalase have an absorption maximum at 400 nm, while Complex I of chloroperoxidase has a maximum at 395 nm.[74,156,157] The complex detected for cytochrome P-450 is analogous to Complex I of cytochrome *c* peroxidase (λ_{max} = 419 nm) [153] and Complex II of horseradish peroxidase (λ_{max} = 420 nm).[156] The second significant difference between the complexes of cytochrome P-450 with hydroperoxides and Complex I of peroxidases and catalyses consists in the kinetics and stoichiometry of their formation[128]. Peroxidases and catalases react with H_2O_2 or hydroperoxides (ROOH) in accordance with 1 : 1 stoichiometry and their reaction is believed to be irreversible. Admittedly very recently it has been shown that the formation of Complex I and Complex II by peroxidases can be a reversible process; Complex I can be reduced to ferri-peroxidase in two stages with the intermediate formation of Complex II when K_2IrCl_6 is used as the reductant[158]. Blake and Coon[128] showed that the interaction of hydroperoxides with cytochrome P-450 is complex and consists of at least two reversible stages:

$$\text{P-450} + \text{ROOH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{C} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{D},$$

where C is the enzyme–substrate complex and D an unstable compound which can be detected spectroscopically according to the authors. The rate constant ratio k_1/k_2 depends greatly on the type of hydroperoxides and is correlated with their hydrophobic properties[128]. It has also been shown that the rate constants k_3 and k_4 are determined by the structure of the peroxides and the spectra of compound D differ for different peroxides, i.e. the nature of the peroxide has a marked influence on the interaction with cytochrome P-450 and on the characteristics of the intermediate compounds. This led White and Coon[12] to the conclusion that the intermediate complex of cytochrome P-450 with ROOH differs from Complex I of peroxidases and catalases. They therefore proposed[12] a new mechanism of the peroxide oxidation differing by the fact that the O–OR bond in the ternary substrate–P-450–ROOH complex undergoes homolytic dissociation and the oxidising agent is the alkoxy-radical RO$^{\cdot}$ derived from the hydroperoxide (Fig.4). The homolytic pathway in the dissociation of the O–OR bond was confirmed in a study of the interaction of cytochrome P-450-LM_2 and R-450$_{cam}$ with phenylperacetic acid[125]. The homolysis of the O–OR bond is supported by the decarboxylation of phenylperacetic acid catalysed by cytochrome P-450:



In the peroxide oxidation mechamism[128] (Fig.4) an important role is attributed to the thiol ligand of cytochrome P-450. The possible involvement of this ligand in the homolytic

decomposition of hydroperoxides was suggested previously by the present authors[139]:

$$ROOH + Fe^{3+}—SH \rightarrow RO^{\cdot} + H_2O + Fe^{3+}—S^{\cdot} .$$

Thermochemical calculation shows that, under favourable solvation conditions, this reaction is entirely feasible close to physiological temperatures[159]. The thiol ligand is in fact an electron donor facilitating the homolytic dissociation of the O–OR bond. The complex formed after the homolysis of the O–OR bond may be equivalent to Complex II of peroxidases and catalases:

$$S^{\cdot}Fe^{2+}OH^{\cdot} \leftrightarrow S^{\cdot}Fe^{3+}OH^{-} \leftrightarrow S^{-}Fe^{3+}OH^{\cdot} \leftrightarrow S^{-}Fe^{4+}OH^{-} .$$

It may be that the intermediate compound detected spectroscopically after mixing ROOH and cytochrome P-450 is in fact Complex II: it is not fortuitous that the absorption maxima of Complex II of peroxidases and of the mixture of cytochrome P-450 with ROOH coincide (at 420 nm).[156]

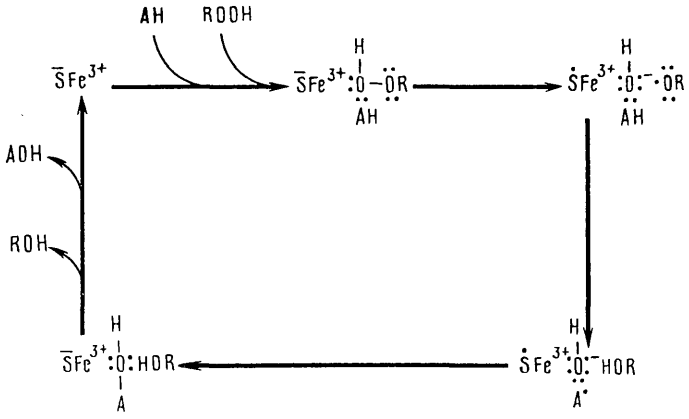


Figure 4.

Without denying the possibility of homolytic decomposition reactions of organic hydroperoxides in the presence of cytochrome P-450, which has been demonstrated in a number of studies[125,139,159], we shall nevertheless make a number of significant comments concerning the interpretation of data obtained by Coon and coworkers[12,128]. Firstly the absorption spectra of Complexes I for peroxidases and cytochrome P-450 need not necessarily be identical and, furthermore, they should in fact differ, since the hydroperoxides become ligands of the haemoprotein, occupying the sixth coordination site, while the fifth axial position contains histidine in peroxidases and cysteine in cytochrome P-450. The differences between the ligands are quite sufficient to account for the difference between the spectra of Complexes I for different haemoproteins. It follows from Table 6 that the nature of the fifth ligand is responsible for the difference between differential absorption spectra of the complexes of ROOH with cytochrome *c* and haemoglobin, on the one hand, and cytochrome P-450, on the other. Secondly, the formation of Complexes I of peroxidases as well as the interaction of ROOH with cytochrome P-450 can be reversible[158]. Thirdly, the oxidation of cyclohexene in the microsomes–TBHP system leads to the formation of epoxycyclohexane, which is inconsistent with the radical process mechanism[100]. Fourthly, the oxidation of labelled acetanilide yielded identical NIH shifts in the complete and hydroperoxide systems, which confirms the similarity of the mechanisms in the two cases. Bearing in mind all the data available at present, one may claim that the hydroperoxide systems involve, apart from the reactions via the oxenoid pathway similar to the reactions in the complete system, also radical processes which are responsible in many instances for the oxidation of certain substrates and the degradation of cytochrome P-450. The processes where the radical stages may predominate include the *N*-dealkylation of tertiary amines, which is effectively retarded by radical process inhibitors (1-naphthol, etc.[69]) and the oxidation of alcohols[14,155]. On the other hand, the oxidation of aromatic compounds and the epoxidation of olefins proceed via the oxenoid pathway, considered in the second section of this review. It is noteworthy that some of the most reactive aromatic compounds can be oxidised simultaneously via two pathways—oxenoid and radical. Benzo[*a*]pyrene is probably oxidised in this way in hydroperoxide systems[165]; the oxenoid reaction pathway leads to the formation of epoxides, while radical processes result in the accumulation of phenols and quinones. The claim[165] that there is a fundamental difference between the mechanisms of the oxidation of benzo[*a*]pyrene in the complete system and with participation of CHP, based on the difference between the reaction products in the two systems, is unduly categorical: we simply have the situation that in the hydroperoxide system yet another reaction pathway (the radical pathway) occurs in addition to the oxenoid pathway.

Other haemoproteins can also catalyse the peroxide oxidation reactions of certain substrates (Table 7), although not all the reactions characteristic of cytochrome P-450 are accelerated by other iron-porphyrins: peroxidase cannot oxidise saturated compounds and alcohols and cytochrome P-450 cannot participate in any of the reactions quoted in Table 7. The question arises how to explain the different reactivities and the differences between the mechanisms of the peroxide oxidation reactions involving different haemoproteins. The first stage of the process is the same for all haemoproteins—the formation of complexes with the peroxides (Table 6). Table 6 does not include data for the known reactions of peroxidases and catalases with hydroperoxides. Complexes of ROOH with different haemoproteins differ in the parameters of the difference absorption spectra—the difference between the axial ligands in the fifth position has an effect. Apart from the axial ligands, the aminoacid residues in the active centres can play an important role in complex formation between ROOH and haemoproteins. It has been suggested that the hydrogen bonds formed between the carboxy-groups of the aminoacids and the distal histidine play a very significant role in the complexes of ROOH with haemoproteins[16] (Fig.5). An important role in the heterolytic cleavage of the O–OR bond in cytochrome *c* by peroxidase has been attributed to the distal histidine-52, arginine-48, and tryptophan-51 [166] (Fig.6). Fig.6 shows that the distal histidine-52 is a kind of acid–base catalyst, the arginine-48 residue stabilises the charge, while the proximal histidine-174 stabilises the haem iron in a high oxidation state, i.e. the active centre of peroxidase is directly involved in the formation of Complex I. It is also known that aspartate-43 of horseradish peroxidase is incorporated via its carboxy-group in the formation of a complex with H_2O_2.[174] In the myoglobin molecule the glycine E8 occupies the same site as aspartate-43 in the horseradish peroxidase molecule and for this reason myoglobin does not form Complex I, in contrast to peroxidase[174]. Thus, despite

the fact that all haemoproteins form complexes with ROOH, not all of them are capable of generating Complex I owing to the differences between the structures of the active centre.

Table 7. Catalytic properties of haemoproteins in the oxidation of organic compounds by peroxides and certain non-peroxide oxidants[16].

Reaction	Haemoprotein exhibiting catalytic activity	References	Haemoprotein without catalytic properties	Ref.
N-Dealkylation of amines	cytochrome P-450 ($ROOH$, H_2O_2)	123, 141-145	cytochrome P-420	123
Ditto	catalase ($ROOH$. H_2O_2)	123	ditto	123
"	peroxidase (H_2O_2)	167	"	123
"	haemoglobin (CHP, H_2O_2)	168	"	123
O-Dealkylation of ethers	cytochrome P-450 (CHP, TBHP, C_6H_5IO)	146-148	haemin, catalase	146
Ditto	ditto	146-148	peroxidase, myoglobin, cytochrome P-420	146
Hydroxylation of aromatic compounds	cytochrome P-450 ($ROOH$, H_2O_2)	100 133-140	haemin, catalase	133
	haemoglobin (CHP)	169	peroxidase, myoglobin, cytochrome b_5, cytochrome P-420	133
	cytochrome *c* (CHP)	163	ditto	133
Oxidation of steroids	cytochrome P-450 ($ROOH$, NaClO, C_6H_5IO, $NaClO_2$)	129 170-173	peroxidase, catalase, metmyoglobin	129
Oxidation of alcohols	cytochrome P-450 ($ROOH$, H_2O_2)	152	peroxidase	152
Ditto	catalase ($ROOH$, H_2O_2)	152	cytochrome *c*	152

*The oxidants employed are indicated in brackets.

The coordination of hydroperoxides at the sixth site in haemoproteins is well known[16,175,176]. The fate of the complexes of hydroperoxides with haemoproteins can be various; peroxidases and catalases form Complex I, while myoglobin does not give rise to such a complex. The formation of radicals in the interaction of certain haemoproteins with hydroperoxides has been demonstrated. The detection of a low-intensity chemiluminescence as a result of the recombination of the peroxy-radicals ROO$^{\cdot}$ showed that such radicals are formed on interaction of hydroperoxides with cytochrome *c*, myoglobin, methaemoglobin, and horseradish peroxidase[177], i.e. in the cases enumerated there is a possibility of radical stages in the oxidation of the substrate introduced into the system. It is at present possible to compare the efficiencies of various haemoproteins in the oxidative dealkylation reactions of *N*-alkylamines and to discuss the differences between the mechanisms of their action (Table 8). Horseradish peroxidase is most effective in the oxidation of amines by hydrogen peroxide[167], while catalase is most effective in the oxidation of DMA by cumenyl hydroperoxide[168]. The radical-cations of the substrate have been detected by EPR in the H_2O_2–peroxidase system on oxidation of aminopyrene[167]. The oxidation of aminopyrene in the CHP–cytochrome P-450 and CHP–myoglobin systems takes place with the same efficiencies and is accompanied by the formation of substrate radicals[178]. Griffin and Ting[179] believe that all the oxidative dealkylation reactions of amines listed in Table 8 proceed via a radical mechanism. Griffin proposed the following mechanism for the oxidative dealkylation of *N*-alkylamines[179]:

$$R_2N{-}CH_3 \xrightarrow[-e^-]{} R_2\dot{N}{-}CH_3 \xrightarrow[-H^+]{} R_2\dot{N}{=}CH_2 \rightarrow \xrightarrow{H_2O} R_2\dot{N}H_2 + H_2C{=}O.$$

A distinctive feature of this mechanism is the radical nature of the process and the incorporation in formaldehyde of an oxygen atom from water and not from an O_2 molecule. We confirmed the radical stages of the reactions in the oxidation of DMA by cumenyl hydroperoxide with participation of microsomes, cytochrome P-450-LM_2,[69] and haemoglobin[168] using 1-naphthol as the radical process inhibitor. The complex nature of the inhibition of the oxidation of DMA by 1-naphthol is consistent with the possible role of radical reactions in the peroxide oxidation with participation of CHP and haemoglobin, catalase, or cytochrome P-450.

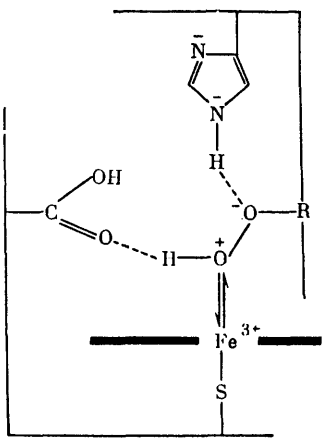


Figure 5.

Thus radical stages are observed in reactions involving the oxidative dealkylation of *N*-alkylamines by hydroperoxides with participation of horseradish peroxidase, myoglobin, haemoglobin, catalase, protohaemin, and cytochrome P-450. In the oxidation of aminopyrine radicals were detected by EPR,[182] while in the oxidation of DMA effective process inhibition by an antioxidant (1-naphthol) was noted[69,168].

We carried out a systematic comparative kinetic study of the oxidation of aniline by cumenyl hydroperoxide with participation of cytochrome P-450,[69,106,136] haemoglobin[169], and cytochrome c.[163] Aniline forms complexes with the three haemoproteins (Table 9). The most stable complexes are formed between cytochrome P-450 and aniline. The difference spectra of the complexes of cytochrome P-450 and cytochrome *c* differ owing to the different nature of the axial ligands in the fifth position (Table 1). An allosteric effect was observed in the interaction of aniline with haemoglobin and the complexes were characterised in this case by three

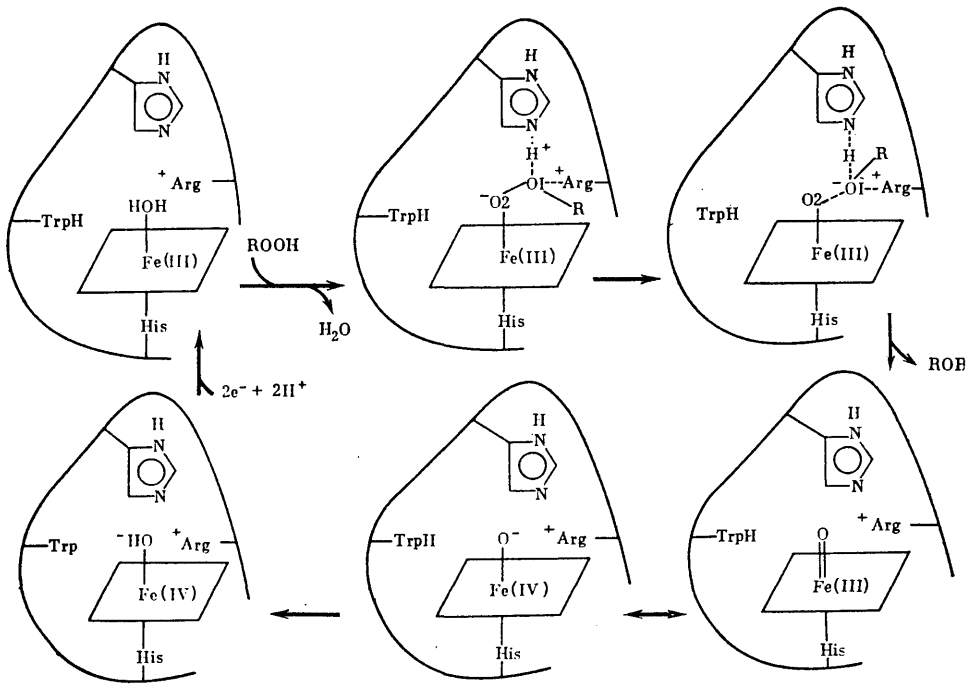


Figure 6.

dissociation constants—K_R, K_T, and K_S. All three haemoproteins catalyse effectively the oxidation of aniline to p-aminophenol. 1-Naphthol inhibits all three reactions, but does not arrest them completely. The reactions involving cytochrome *c* and haemoglobin have a radical mechanism, whereas in our view the reactions catalysed by cytochrome P-450 may involve not only radical stages but also the oxenoid pathway[69].

Table 8. Systems for the oxidative dealkylation of *N*-alkylamines exhibiting features of radical reactions.

Haemoprotein	Oxidant	Substrate	References
Horseradish peroxidase	H_2O_2	aminopyrine	167, 179
Ditto	"	DMA	180
"	"	DPT	180, 181
Metmyoglobin	H_2O	aminopyrine	179
Metmyoglobin	CHP	aminopyrine	182
Methaemoglobin	H_2O_2	DMA	168, 180
Methaemoglobin	H_2O_2	DPT	180
Methaemoglobin	CHP	DMA	168
Catalase	CHP	DMA	168
Protohaemin	H_2O_2	aminopyrine	179
Cytochrome P-450 from rabbit liver PB-microsomes	CHP	aminopyrine	178
Rat liver microsomes	CHP	DMA	168
Rabbit liver PB-microsomes	CHP	DMA	69
Cytochrome P-450-LM_2 from rabbit liver PB-microsomes	CHP	DMA	69

Note. DPT = *N*,*N*-dimethyl-*p*-toluidine; PB denotes microsomes induced by phenobarbital-sodium.

Table 9. Spectroscopic parameters of the complexes of aniline with haemoproteins.

Haemoprotein	λ_{max}, nm	λ_{min}, nm	K_S, mmol litre^{-1}	References
Cytochrome P-450:				
in PB-microsomes	431	398	0.60	160
in MC-microsomes†	431	399	0.027	160
in microsomes	429, 440	385, 397	0.160	160
P-450-LM_2 from rabbit microsomes	433	412	3.230	162
P-450-LM_4 from rabbit microsomes	427	391	1.430	162
Cytochrome *c*	421—417	401—399	24—13	183
Ditto	420	405	24*	163
Human haemoglobin	425	405	K_R 75 K_T 260 K_S 105	30
Horse haemoglobin	425	405	K_R 33 K_T 125 K_S 53	164

*Value obtained at pH 5.8; the remaining values of K_S for the aniline–cytochrome *c* complex were obtained at different pH.

†MC = 3-methylcholanthrene (Editor of Translation).

The hydroperoxide oxidation reaction of DMA is inhibited by a $CuCl_2$ and the copper complexes of lysine and tyrosine[144]. The inhibition of the oxidation of DMA by $CuCl_2$ in the reaction involving CHP and cytochrome P-450-LM^2 is non-competitive, while the copper complexes of lysine and tyrosine inhibit this process via a mechanism of the mixed type. The inhibiting effect of copper compounds on the oxidation of

DMA by cumenyl hydroperoxide can be explained by the decomposition of the hydroperoxide via the Haber–Weiss reaction with formation of the radicals $RO^{\cdot}$ and $RO_2^{\cdot}$, which causes the degradation of cytochrome P-450. Copper chloride at concentrations of ~0.001 M and above denatures cytochrome P-450 in the absence of CHP.[144]

The similarities and differences between the hydroperoxide oxidation reactions with participation of cytochrome P-450 and other haemoproteins can be discussed on the basis of the data presented in this section[16,18]. These processes are characterised by the following sequence of reactions:

$$Fe^{3+} + ROOH \rightleftarrows Fe^{3+}(H)-O-OR \quad ; \qquad (4)$$

$$Fe^{3+}(H)-O-OR \rightarrow [Fe^{3+}O] + ROH \quad ; \qquad (5)$$

Complex I

$$Fe^{3+}(H)-O-OR \rightarrow Fe^{2+} + H^+ + RO_2^{\cdot} \quad ; \qquad (6)$$

$$Fe^{3+}(H)-O-OR \rightarrow [FeOH]^{3+} + RO^{\cdot} \quad ; \qquad (7)$$

$$[Fe^{3+}O] + AH \rightarrow Fe^{3+} + AOH \qquad (8)$$

$$[Fe^{3+}O] + AH \rightarrow [Fe^{2+}O] + A^{\cdot} + H^+ \quad ;$$

Complex II

$$[Fe^{2+}O] + AH \xrightarrow{H^+} Fe^{3+} + A^{\cdot} + H_2O \quad . \qquad (10)$$

As already mentioned, all haemoproteins (with the exception of cytochrome P-450-LM_4) form complexes with ROOH [reaction (4)]. Peroxidases, catalases, and cytochrome P-450 subsequently form Complex I [reaction (5)]. Myoglobin, haemoglobin, and cytochrome *c* apparently do not form Complex I owing to the differences between the structure of the active centre and the structures of peroxidases, catalases, and cytochrome P-450. The formation of Complex I (where this occurs) is accompanied by the simultaneous reactions involving the decomposition of the complexes of haemoproteins with ROOH into radicals [reactions (6) and (7)]. All haemoproteins without exception can generate the radicals $RO^{\cdot}$ and $RO_2^{\cdot}$, which are capable of oxidising the majority of substrates of monoxygenases and can decompose the porphyrin ring in haemoproteins[16,159]. Reaction (5), on the one hand, and reactions (6) and (7), on the other, depend on the type of haemoprotein. Reactions (6) and (7) predominate for myoglobin, haemoglobin, and cytochrome *c*, while reaction (5) is the main one for cytochrome P-450, peroxidases, and catalyases, i.e. one group of haemoproteins (myoglobin, haemoglobin, and cytochrome *c*) decompose hydroperoxides via the homolytic mechanism, while the other group (cytochrome P-450, peroxidases, and catalases) cleave the O–OR bond mainly via the heterolytic mechanism with formation of Complex I. The presence of the substrates of cytochrome P-450 (aniline, DMA, and naphthalene) and radical reaction inhibitors (1-naphthol and substituted phenols) suppresses reactions (6) and (7) and promote the specific enhancement of reaction (5).[16,139]

The mechanism of the oxidation of Complexes I is determined, in the first place, by the nature of the haemoprotein and, in the second place, by the nature of the substrate. Complex I of peroxidases and catalases is characterised by the presence of an iron ion in a high oxidation state (Fe^{4+}) and is distinguished by its ability to undergo one-electron oxidation processes, since it is a radical [reaction (9)]. Reaction (9) results in the formation of Complex II, which oxidises in its turn yet another molecule of the substrate AH. The activity of Complexes I of peroxidases and catalases is fairly high and these complexes readily oxidise a multiplicity of substrates—phenols, amines, etc.[27,28], but cannot rupture the strong C–H bonds of saturated hydrocarbons, which are not substrates of peroxidases and catalases.

Complex I of cytochromes P-450 is capable of undergoing simultaneously two-electron oxidation reactions (with the oxenoid or hydroxylase mechanism) and one-electron oxidation reactions (with the radical or peroxidase mechanism). Presumably the reactivity of Complex I of cytochromes P-450 is higher than the reactivity of the same complex of peroxidases and catalases, i.e. the iron ion in Complexes I of cytochrome P-450 can exist in a higher oxidation state than the iron ion in Complexes I of peroxidases and catalases. The highest oxidation state of iron in Complex I of cytochrome P-450 is stabilised not only by the porphyrin ring, as in peroxidases[73,74], but also by the thiol ligand in the fifth coordination site. The main difference between cytochrome P-450 and other haemoproteins, responsible for its unique properties, consists in the possibility of the stabilisation of Complex I via two pathways—with participation of the porphyrin ring and the thiol ligand. The relative contributions of the radical and heterolytic stages in oxidation by Complex I of cytochrome P-450 are determined by the nature of the substrate: *N*-alkylamines, saturated hydrocarbons, ethers, and alcohols are oxidised by the radical mechanism, while aromatic compounds and olefins are oxidised mainly via the oxenoid heterolytic pathway, i.e. with the transfer of two electrons from the substrate to Complex I simultaneously. Naturally, in many instances there is a possibility of the simultaneous occurrence of the one- and two-electron oxidation reactions. This probably happens in the oxidation of benzo[*a*]pyrene and cyclohexene by hydroperoxides: the epoxyarene derivatives of benzo[*a*]pyrene and epoxycyclohexane are formed via the oxenoid mechanism, while the phenols derived from benzo[*a*]pyrene and 2-cyclohexanol are formed via the radical mechanism. Tertiary amines readily give up an electron to many oxidants and are therefore oxidised mainly via the radical mechanism, which has been proposed and proved by Griffin[179], with the intermediate formation of the relatively stable iminium cation $R_2\overset{+}{N}=CH_2$, which is converted into a secondary amine and formaldehyde in an aqueous medium.

Table 10 summarises the available information about the nature of the oxidation of different substrates by peroxides with participation of various haemoproteins. We have divided haemoproteins into three groups: the reactions of myoglobin, methaemoglobin, and cytochrome *c* *proceed only via the radical pathway* with participation of the radicals $RO^{\cdot}$ and $RO_2^{\cdot}$, the second group of haemoproteins—peroxidases and catalases—catalyse reactions via the radical mechanism with formation of Complexes I of these proteins, and finally the third group consists of cytochromes P-450, which, depending on the nature of the substrates, can convert them via the heterolytic pathway with participation of Complexes I {cyclohexene, naphthalene, aniline, and benzo[*a*]pyrene} or via the radical pathway with participation of the same Complex I and the radicals $RO^{\cdot}$ and $RO_2^{\cdot}$ (DMA, aminopyrine, cyclohexane, cumene, ethylbenzene, alcohols, and camphor).

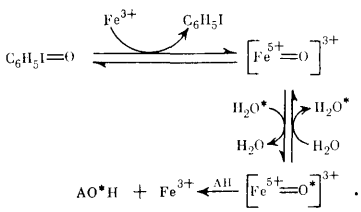
Table 10 shows that there are substrates with "amphoteric" properties, capable of being oxidised simultaneously via two pathways—the homolytic and heterolytic pathways {benzo[*a*]pyrene and possibly other aromatic hydocarbons}. It follows from the data presented here that there is no universal mechanism of the catalysis of the peroxide oxidation by haemoproteins. The mechanism of the peroxide reactions of haemoproteins is determined by several factors:

1. The nature of the haemoprotein, the structure of its active centre, and the fifth axial ligand.
2. The nature of the substrate oxidised, its ability to undergo one- or two-electron redox reactions, and the strength of the C–H bonds dissociated in hydrocarbons or the oxidation-reduction potential of *N*-alkylamines.
3. The nature of the oxidant employed.

Table 10. Reactions in ROOH–haemoprotein systems.

System	Possible oxidising agents	Substrate	
		one-electron reactions	two-electron (oxenoid) reactions
Myoglobin + CHP	$RO^{\cdot}$, $RO_2^{\cdot}$	aminopyrine [182]	none
Haemoglobin + CHP	ditto	aminopyrine [182]	none
Ditto	»	aniline [169]	none
»	»	DMA [168]	none
Cytochrome *c* + CHP	»	aniline [163]	none
Peroxidase + H_2O_2	$[Fe^{3+}O]$	aminopyrine [167]	none
Ditto	ditto	DMA [180]	none
Catalase + CHP	»	DMA [168]	none
Cytochrome P-450 from liver microsomes + ROOH	$[Fe^{3+}O]$, $RO^{\cdot}$, $RO_2^{\cdot}$	DMA [69]	cyclohexene [100]
Ditto	ditto	aminopyrine [178]	naphthalene [100]
»	»	cyclohexane [125]	aniline [69]
»	»	cumene [125]	—
»	»	ethylbenzene [125]	—
»	»	benzo[*a*]pyrene [165]	benzo[*a*]pyrene [165]
»	»		—
Cytochrome $P\text{-}450_{cam}$ + phenylperacetic acid	$[Fe^{3+}O]$, $RO^{\cdot}$, $RO^{2\cdot}$	alcohols [152] camphor [125]	—

The last postulate has been confirmed by the different behaviour in oxidation reactions with participation of cytochrome P-450 of oxidants such as hydrogen peroxide, organic hydroperoxides[12,128], and iodosobenzene[184]. It has been shown recently that, in the oxidation of camphor by iodosobenzene with participation of cytochrome $P\text{-}450_{cam}$ using $H_2{}^{18}O$, the oxygen incorporated in the oxidation product originates from water and not from the oxidant[184]. The authors[184] suggest that in the presence of $P\text{-}450_{cam}$ iodosobenzene forms a unique oxenoid capable of exchanging its oxygen rapidly with that of water:



In the absence of cytochrome $P\text{-}450_{cam}$, there is no isotope exchange between iodosobenzene and water. In our view, there is a possibility of another mechanism which explains the results of the above study: cytochrome P-450 catalyses the decomposition of iodosobenzene with formation of an oxygen atom, whose high reactivity explains its rapid isotope exchange with $H_2{}^{18}O$. The hydroxylating agent may be the ^{18}O atom, which exhibits a high hydroxylating capacity[18].

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In conclusion one should note that the final determination of the mechanisms of the catalytic action of haemoproteins in oxidation reactions requires further studies of several different kinds: comparative investigation of the oxidation of a wide range of substrates with participation of different haemoproteins under comparable conditions and the search for new approaches to the study of the intermediate stages in processes with participation of cytochrome P-450 in order to elucidate the nature and structure of the hydroxylating agent. The determination of the nature of the active species in microsomal oxidation will lead to new possibilities for a specific search for simple catalytic chemical systems capable of replacing a unique haemoprotein, namely cytochrome P-450, and for devising oxidation processes which will not be inferior in their efficiency and selectivity to enzymatic processes.

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Kinetics of Gas-phase Ion-Molecule Exchange Reactions

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The kinetics of ion-molecule exchange reactions (IMR), which are important in high-energy and analytical chemistry, are discussed, and their special features and the factors influencing the reaction rate are analysed. Special attention is paid to slow IMR with rate constants substantially smaller than the gas-kinetic ion-molecule collision rate.
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I. INTRODUCTION

The foundations of the kinetics of gas-phase ion-molecule reactions (IMR), a new branch of chemical kinetics, were laid by Tal'roze[1,2]. Since then, interest in IMR has grown very considerably as a result of new developments in radiation chemistry, the physics and chemistry of plasmas and of gas discharges, the chemistry of planetary ionospheres and of interstellar clouds, and other systems in which the molecular composition of an ionised medium is determined mainly by IMR[3-6].

Ion–molecule reactions play an important role in analytical techniques, especially in mass spectroscopy, because they yield simple line spectra which facilitate the analysis of complex organic compounds and their mixtures and from which information on the structure and the energy state of the ions can be obtained[7-10].

Methods based on the study of IMR offer important information on the acid-base properties of molecules in the gas phase: their proton and electron affinity[11,12], the mechanism by which the ions become solvated in a liquid, and the mechanism of the gas-liquid phase transition.

Ion-molecule reactions are a convenient way of experimentally identifying and studying the special features of the elementary chemical acts, and the fundamental nature of the reactivity of the system.

The reacting ions can be obtained relatively simply with different energy distributions (controlled by varying the energy of the ionising radiation) in IMR. An electric field can be used to vary the kinetic energy of the reacting ions and to analyse the resulting ions in terms of their energy. Both the reacting and the resulting ions can be separated and monitored very effectively by mass-spectrometric methods. IMR can be studied without difficulty at flow rates of the order of one ion per second by existing experimental techniques. The sensitivity and selectivity of the method are sufficient to justify detailed studies of IMR under non-equilibrium conditions (which are far less easily undertaken in the case of neutral reacting species). These features of the method explain the important contribution of IMR data to recent developments in the theory of elementary processes.

Experimental methods used in quantitative studies of IMR are fully reviewed in a recent monograph[17], and we shall only discuss a few special aspects of the technique in this review. In the internal ionisation methods[20] both the primary ion and the secondary (product) ion are obtained within the ionisation chamber of the ion source of a mass spectrometer. The most detailed information on the initial vibrational energy distribution of the primary ions is obtained by using photon impact ionisation[21-25]. The pulse method[26], in conjunction with ion trapping[27-30] and ion cyclotron resonance (ICR)[31-34] techniques, allows the reactions of thermal ions to be studied at low pressures. At relatively high pressures other methods are used (plasma decomposition in a flow[35] and ion drift in an electric field[37]).

In the external ionisation methods the primary ions are introduced into the ionisation chamber from outside[20,38-40], thus allowing the kinetic energy of the ion to be determined. These methods include the crossed beam method[41-44], which is particularly convenient for measurements of the angular distribution of the products. Information on the internal energy and structure of the primary ions is obtained by analysing the radiation[45,46], by impact spectroscopy methods[47,48], and by analysing the radiolysis products of gases and of condensed phases.

Several monographs dealing specifically with various aspects of IMR have appeared in recent years[13-19]: the aim of the present review is to examine some of the factors affecting the rate of bimolecular IMR and the kinetics of the elementary processes in these reactions.

II. METHODS OF CALCULATING THE KINETIC PARAMETERS

Mutual polarisation plays an important role in the collision between an ion and a molecule. The Langevin formula can be used to allow for this effect in the expressions for the rate constant and the cross section of ion-molecule collisions[50]:

$$k = 2\pi e(\alpha/\mu)^{1/2} \quad (1)$$

$$\sigma = \pi e(2\alpha/E)^{1/2} \quad (2)$$

where α is the polarisability of the molecule, e is the charge on the electron, μ is the reduced mass, and E is the kinetic energy of the relative motion of the ion and the molecule. When an ion interacts with a molecule which has a constant dipole moment an upper limit for the collision rate can be obtained by the formula[51,52]

$$k = 2\pi e\mu^{-1/2}[\alpha^{1/2} + \mu_D(2/\pi k_B T)^{1/2}] \quad (3)$$

where μ_D is the dipole moment, k_B is Boltzmann's constant,

and T is the absolute temperature. Methods of calculating the rate constants of collisions between ions and atoms (or molecules) with allowance for electronic polarisation, dipole orientation, ion–quadrupole forces, and interactions between induced dipoles are reviewed in a recent monograph[51]. It is often found that the rates of exothermic or thermoneutral exchange IMR are close to the corresponding ion–molecule collision rates[53].

The efficiency of the exchange reaction depends on the shape of the multidimensional potential energy surfaces for the system of colliding particles and on the probability of transitions between these surfaces. Exact calculations of the potential surfaces and of the cross-sections of IMR have been attempted only for very simple systems[54,55].

We shall confine our discussion to the factors directly related to the parameters of the reactants and able to influence the effectiveness of the reactions. The first calculation of the rate constant of an IMR was reported by Eyring and coworkers[56], who applied to the reaction

$$H_2^+ + H_2 = H_3^+ + H \qquad (4)$$

a variant of the transition state method in which only long-range attractive forces are considered, and the effective activation energy is assumed to be determined by the competing effects of the centrifugal force and the attractive force between reactants due to the polarisation of the neutral species. In this model of the interaction, the distance between the reacting species in the activated complex is large, and the rotation of the two reacting particles can be treated as the rotation of uncoupled partners. The vibrational degrees of freedom are assumed to be the same as for the isolated reactants (the molecule and the ion). Therefore the vibrational and the rotational partition functions of the reactants and of the activated complex are simplified in the expression for the rate constant of the reaction, and the rate constant of an exothermic reaction is defined by Eqn.(1) and is equal to the rate constant of the ion–molecule collision process.

We should stress that the first strict calculation[57] of the rate constants of IMR with zero activation energy by the transition state theory appeared in 1978, i.e. many years after Eyring's original paper[56].

Most of the specific calculations of cross sections and rate constants for IMR have relied on the statistical theory, which is particularly convenient for non-activated reactions. This theory assumes strong interactions between all the degrees of freedom in the intermediate complex, making the decomposition of the intermediate complex in any direction allowed by the conservation laws equally probable. The first step in the reaction is the formation of the intermediate complex, within which the energy and momentum of the reactants become statistically distributed over all degrees of freedom up to the instant of decomposition; the second step consists in the decomposition, which depends only on the total energy and momentum, and is independent of the other initial conditions under which the complex was formed.

The statistical theory was first applied to IMR by Tal'roze and Firsov[58,59] in a simplified form which did not allow for conservation of the total momentum, but it was subsequently further developed and expanded[60,61]. In all the calculations the exothermic and thermoneutral IMR were assumed to have zero activation energy, and the rate constant for the formation of the intermediate complex was identified with the rate of ion-molecule collisions. A valuable feature of this variant of the statistical theory is the small number of parameters (relating only to the reactants and products, and not to the collision complex) needed to calculate the full set of characteristics of the elementary act of the IMR.

The statistical theory has been used to calculate the dependence of the rate constants and cross-sections of IMR on the translational and internal energy of the reactants[62,63] and the energy distribution of the products of the IMR.[63,64]

The application of the statistical theory to IMR has been discussed by several reviewers[63,65,66], and the agreement between calculation and experiment has been shown to be good. For example, the steeper fall in the cross-section of exothermic IMR with increase in the kinetic energy of the ions [as compared with the effect predicted by formula(2)] can be explained in terms of the statistical theory by the competing effect of the backward decomposition of the intermediate complex into the initial reactants[58]. The reaction cross-section falls more steeply when the secondary ion can dissociate[67]. The subsequent decomposition reactions can also be described by the statistical theory.

In some systems serious discrepancies are observed between experiment and calculations by the statistical theory. For example, collisions of the type of

$$CH_3CDO^+ + CD_3CDO \rightarrow H_3C{-}C\begin{matrix}O\cdots D\\ +\\ D\cdots O\end{matrix}C{-}CD_3$$

produce a symmetrical complex which should (according to the statistical theory) yield CD_3CDOD^+ and CH_3CDOD^+ as products with equal probabilities. Experimentally[68] we find that CD_3CDOD^+ is formed preferentially, suggesting that the charge in the complex has not been fully delocalised.

Reported differences between calculation and experiment may be due to the following factors:

1) the probability of formation of the intermediate ion–molecule complex is not unity (as is assumed in the theory),

2) the exchange of energy between the different degrees of freedom in the complex is hindered,

3) the potential surface of the IMR includes an energy barrier.

To allow for these factors we need to formulate the theory of IMR in greater detail, and to introduce additional parameters. For exothermic IMR taking place without activation through a "soft" polarisation complex the statistical theory and the activated complex theory give identical results.

In the case of endothermic IMR the statistical theory is applicable only when the collision complex has a stable configuration. For example, the reaction

$$C^+ + H_2 \rightarrow CH_2^+ \rightarrow CH^+ + H \qquad (5)$$

can form the strongly bound complex CH_2^+, whereas the H_4O^+ complex formed in

$$H_2O^+ + H_2 \rightarrow H_3^+ + OH \qquad (6)$$

is unstable. The statistical theory satisfactorily describes the dependence of the cross-section on the kinetic energy near the threshold for reaction (5), but for reaction (6) the same calculation gives unacceptable results[69,70].

Reaction (6) can be described by the activated complex theory on the assumption that the energy threshold is shifted towards the reactants[70]. In general, the activated complex theory is most successfully applied to reactions with a threshold energy when these are "direct" processes, i.e. reactions in which the interaction time of the reactants is small compared to the characteristic time of the redistribution of energy over the degrees of freedom of the system.

The validity of the activated complex theory or of the statistical theory when applied to a specific reaction is determined by the ratio of the height of the energy barrier corresponding to the transition state to the depth of the potential well corresponding to the intermediate complex. A recently developed unified statistical model yields a generalised expression for the rate constant of the reaction which can be

used for direct reactions as well as for reactions taking place through a long-lived complex[71]. This model has not yet been used in the calculations for IMR.

III. STERIC FACTORS AND TEMPERATURE EFFECTS

The low rate constants of some exothermic IMR (as compared to the values predicted by the statistical theory) have been ascribed[72] to the need for a particular mutual orientation of the colliding particles to allow chemical rearrangement in the ion–molecule complex. The following expression is obtained for the differential collision cross-section of the ion and the molecule with an orbital quantum number L:

$$\sigma(L, E) = (2L+1)\pi\hbar^2/2\mu E \ .$$

Noting that only one of the $(2L+1)$ possible projections of the vector for the momentum of the relative motion of the reactants leads to reaction, and that the maximum value L^* is determined by the Langevin capture cross-section according to the formula

$$L^*(L^*+1) = 8\mu^2\alpha e^2 E)^{1/2}\hbar^2$$

for the full cross-section of the reaction produced by the collision of the reactants, we arrive at

$$\sigma(E) = \pi\hbar(\alpha e^2/2\mu^2 E^3)^{1/4} \qquad (7)$$

so that the rate constant is

$$k(E) = \pi\hbar(2\alpha e^2/E)^{1/2}/\mu \ . \qquad (8)$$

In the case of a Maxwellian distribution of the velocities of the reacting particles at temperature T the expression for the rate constant becomes

$$k(T) = 3.2(2\alpha e^2/k_B T)^{1/2} \ . \qquad (9)$$

In the case of IMR involving symmetrical reactants the right-hand sides of Eqns.(7)–(9) should be multiplied by the degeneracy factor g, Thus, for the reaction

$$CF^+ + C_3F_8 = CF_2 + C_3F_7^+ . \qquad (10)$$

we have $g = 8$, since any one of the eight fluorine atoms in the C_3F_8 molecule can act as a reaction centre. The calculated[72] rate constant of reaction (10) is 5.2×10^{-11} cm^3 s^{-1}, and the Langevin collision rate constant of the reactants is 1.08×10^{-9} cm^3 s^{-1}. The experimental value[73] of the rate constant for this reaction is 3.7×10^{-11} cm^3 s^{-1}, in good agreement with the calculated value[72]. In IMR in binary mixtures of ethylene and fluorinated ethylenes the rate of the condensation reactions giving $C_3(H,F)_5^+$ and $C(H,F)_3^+$ as products has been shown[74] to be very sensitive to the replacement of H atoms by F atoms. In the $C_2H_4^+ + C_2H_4$ system every collision leads to interaction, whereas in the $CF_2CH_2^+ + CF_2CH_2$ system the rate constant of the corresponding reaction is less than 10^{-12} cm^3 s^{-1}. The presence of the fluorine atoms does not make the reaction thermodynamically forbidden, but it increases the height of the barriers opposing the migration of atoms (H, or F) in the intermediate complex. The high rate constants of reactions similar to (10) but involving hydrocarbons have been explained[72] in terms of the relatively high mobility of H, H^+, and H^- in the intermediate complex (as compared to the mobility of the fluorine atom).

Fast IMR involving the transfer of a fluorine atom have been recently discovered experimentally[75]:

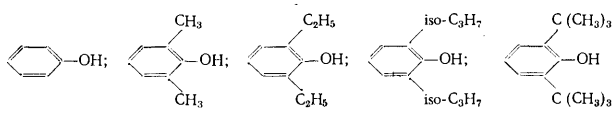
$$CH_3^+ + CH_2F_2 \rightarrow CH_3F^+ + CH_3F$$
$$CH_3^+ + CHF_3 \rightarrow CH_3F + CHF_2^+$$
$$CH_3^+ + CF_4 \rightarrow CF_3^+ + CH_3F \ .$$

The rate constants of these reactions calculated by formula (8) are much lower than the experimental values. Evidently, the validity of formulae (7)–(9) in calculations of the kinetic parameters of IMR must be limited by a number of factors (not merely the mass of the migrating atom). Thus in the collision between an ion and a molecule some of the energy of the relative motion may be converted into vibrational or rotational energy of the reactants, giving a complex in which the reactants can experience many intramolecular collisions. For example, according to the activated complex theory[57] the ion-atomic and a diatomic particle at 300 K and with a potential well of 2 eV gives a complex with a life time equivalent to 100 vibrations (vibration period 3×10^{-13} s). The complex formed by two diatomic species for the same parameters is even longer-lived (3×10^3 vibrations), thus increasing the probability of acheiving a mutual orientation of the reactants favourable to the reaction. However, we should stress that the number of intra-complex conditions is greater in the $CH_3^+ \ldots CH_2F_2$ than in the $CF^+ \ldots C_3F_8$ system. At present formulae (7)–(9) have been shown to be consistent with experiment only for IMR between neutral and charged unsubstituted fluorocarbons.

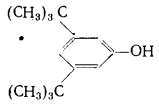
Orientation effects are even more important when the collision has to be followed by the transfer of a large group of atoms (as opposed to the transfer of a single atom). An example is the transfer of the acetyl ion[76], in which the reacting ion is formed by the reaction

$$CH_3COCOCH_3^+ + CH_3COCOCH_3 \rightarrow (CH_3CO)_3^+ + CH_3CO \ .$$

Bursey and coworkers have shown[76] that in the phenol series



the acetylation reaction takes place only with the first three members: the last two compounds do not react because the approach of the $C_6H_9O_3^+$ ion and the transfer of the acetyl ion are sterically hindered. The role of the steric effect is confirmed by the observation that the phenol



(in which the methyl groups are remote from the reaction centre) is readily acetylated[77]. Thus even in the ion–molecule collision of complex multi-atomic particles, which can be expected to produce a long-lived collision complex, the exothermic IMR may be found to be slow as a result of steric effects opposing the formation of an intermediate reactive complex with strong interactions between the degrees of freedom responsible for the chemical regrouping of the atoms.

These (and other similar) experimental results have led to the realisation that ion–molecule complexes must be classified into two distinct types. The collision between an ion and a molecule can give rise to a "soft" complex, in which the reactants are bound by relatively weak polarisation forces and remain relatively far apart, so that energy and mass exchange in the complex are hindered. Such a complex can either dissociate back into its initial reactants or be converted into a "hard" complex, characterised by a strong chemical bond between the reactants. The "hard" complex can be treated in terms of the statistical theory to calculate the relative probabilities of alternative decomposition paths.

The need to distinguish between two types of complex is evident also from the temperature dependence of the rate constants of IMR. Thus, a study[78,79] of the transfer of the

hydride ion from isobutane to s-$C_3H_7^+$ has revealed the existence of two temperature regions, with different temperature dependences of the rate constant. At high temperatures the rate constant has a negative temperature coefficient, and at low temperatures it becomes independent of temperature and equal to the Langevin limiting value. This temperature dependence can be explained by postulating the following scheme:

$$R_1^+ + R_2H \underset{k_b}{\overset{k_c}{\rightleftarrows}} [R_1^+ \ \ldots \ R_2H]_{soft} \xrightarrow{k_T} [R_1 \ldots R_2H]^+_{hard} \rightarrow \text{products} .$$

It is assumed[78,79] that the rate constants for the formation (k_C) and for the back dissociation (k_b) of the soft intermediate complex are independent of temperature whereas the rate constant of the transition from the soft to the hard complex (k_T) is a function of temperature. This dependence was calculated by the activated complex theory for bimolecular reactions, assuming that the activation energy is zero and that only the pre-exponential factor is temperature-dependent:

$$A(T) = \gamma T^{-(2+r/2)} \qquad (11)$$

where γ is temperature-independent and r is the number of internal rotators in the reacting molecules which are converted into oscillators in the activated complex (performing torsional vibrations). For example, from the temperature dependence of the rate constant of the reaction

$$t\text{-}C_4H^+_9 + iso\text{-}C_5H_{12} \rightarrow C_5H^+_{11} + C_4H_{10} \qquad (12)$$

we obtain (experimentally) $r = 2$. This means that the formation of the activated complex of reaction (12) is accompanied by the disappearance of two internal rotators (probably methyl groups, since the rotation of these groups can be strongly hindered in an activated complex). According to the structural formulae of the reactants the maximum number of rotators which may become hindered is six. Thus the model (in conjunction with experimental data on the temperature dependence of the rate constant) offers valuable information on the properties of the activated complex for IMR.

In some reactions the experimental temperature coefficient is even smaller than the value expected from the number of hindered rotators according to the above model. The temperature dependence of the rate constant for the reaction

$$CH_4D^+ + CH_4 \rightarrow CH_5^+ + CH_3D$$

has been explained[80] by postulating a model which assumes the existence of a soft and a hard complex but allows the rate constant of the backward decomposition of the soft complex into the initial reactants to be temperature-dependent. This model is free from the stringent limitations imposed on the temperature coefficient by the number of hindered rotators, but it includes some parameters which cannot easily be calculated theoretically (for example, the life time of the soft complex). The results of experiments under non-equilibrium conditions have also been explained by this qualitative model. For example, in IMR of s-$C_3H_7^+$ with iso-butane, normal butane, pentane, and hexane the rate constant for the exchange of a hydride ion is much lower in the pure vapours than in mixtures (which are diluted with molecules not involved in the interaction with the reactant ion[81]). This difference has been ascribed[81] to decrease in internal energy of the reactant ion resulting from the increased number of collisions with molecules of the buffer gas prior to the reaction. The characteristic time of the backward decomposition decreases as the excitation energy of the soft complex increases, and therefore the probability of the exchange reaction decreases: it is assumed that the rate constant for the conversion of the soft complex into a hard complex is weakly dependent on the excitation energy.

The rate constant for the formation of the soft complex is not always equal to the Langevin limit. According to measurements of the rate constant of associative IMR the high-pressure limit[82] for the formation of the soft complex can be much lower than the rate constant of the ion-molecule collisions. Collision may be followed by reflection or rapid back-dissociation of the complex into the reactants during a single vibration if the relative kinetic energy of the reactants cannot be accommodated in internal degrees of freedom of the ion-molecule complex during the collision. No theoretical calculations of the efficiency for the formation of soft complexes during ion-molecule collisions have yet been reported.

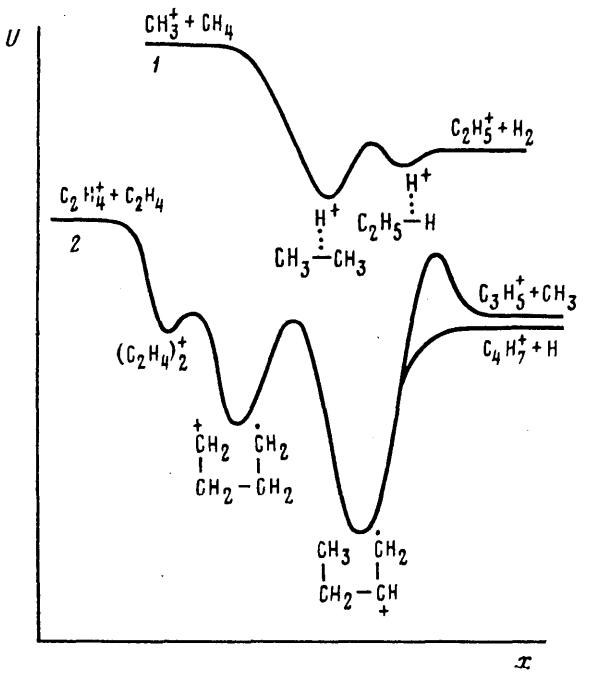


Figure 1. Profiles of the reaction paths $CH_3^+ + CH_4 \rightarrow C_2H_5 + H_2$ [85] (*1*) and $C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$ [86] (*2*); U is the potential energy, x is the reaction co-ordinate.

The potential curve for the formation of ion-molecule complexes of two types in processes such as

$$A^+ + B \rightleftarrows AB^+ \rightleftarrows CD^+ \rightarrow C + D^+ \qquad (13)$$

has two minima, separated by a small barrier. In the state AB^+ the system has enough energy to be converted into the state CD^+, or to decompose into the initial reactants. The potential barrier opposing the reverse dissociation into A^+ and B is high, but under these conditions the pre-exponential factor in the expression for the rate constant is also large, and the decomposition of the soft complex (AB^+) takes place through a soft transition state. On the other hand the potential barrier to the transition of AB^+ into the hard complex CD^+ is relatively small, but the transition takes

place through a hard transition state and therefore the pre-exponential factor is small[83]. This model accounts for the low efficiency and negative temperature coefficient of the rate constants of isotope exchange reactions of the type of

$$CD_3\overset{O}{\overset{\|}{C}}CD_2^- + CH_3\overset{O}{\overset{\|}{C}}CH_3 \rightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2^- + CD_3\overset{O}{\overset{\|}{C}}CD_2H$$

$$^{37}Cl^- + CH_3{}^{35}Cl \rightarrow {}^{35}Cl^- + CH_3{}^{37}Cl$$

and allows us to calculate the height of the barrier separating the soft from the hard complex. The concept of a soft and a hard complex can also be used to explain the effect of temperature and pressure on the kinetics of IMR.[84]

Some ion-molecule systems can include several types of hard complex, or they may not have a complex of either type. Information on the form of the potential surface along the reaction co-ordinate can be obtained from data on ion-molecule equilibria[85] and from experiments on the photo-ionisation of the van der Waals molecular complexes[86]. Typical potential energy profiles are shown in Fig.1.

IV. PATH PROFILES AND KINETIC FEATURES OF IMR

Statistical methods of calculation assume a quasi-equilibrium distribution of the reaction products in excitation energy, but substantial departures from equilibrium are often observed in experiments. If the shape of the potential energy surface is known, both the reaction cross-section and the distribution functions of the products in excitation energy can be obtained from calculations by the dynamic method[87]. This method is usually applied to a linear reaction of the type of

$$A + BC \rightarrow AB + C$$

whose potential energy surfaces do not include deep potential wells. In this case the reaction takes place without the formation of a long-lived intermediate complex. The largest non-equilibrium effects can be expected in these direct reactions. The probability of the reaction can be calculated (for each trajectory) by the classical equations of motion. The energy distribution over the degrees of freedom of the products is very sensitive to the mass ratios of the atoms A, B, and C, and to the shape of the potential energy surface. For example, if the evolution of energy in an exothermic reaction takes place during the ejection of the products the energy of the reaction appears as kinetic energy of the products, but if the evolution of energy takes place during the approach of the reactants a higher proportion of the energy of the reaction will appear as vibrational energy of the product molecule AB.

Calculations by the dynamic method for the potential energy surfaces of exothermic reactions with a potential barrier show that the barrier can be surmounted by the kinetic energy of the reactants if it is located in the region of the reactants. On the other hand if the barrier is displaced towards the reaction products it is surmounted by the vibrational energy of the reactant.

Non-empirical calculations of the potential energy surface are extremely laborious even for the simplest systems, and they require a large number of approximations which can seriously degrade the precision of the result[55,87]. For this reason the most successful methods so far have been semi-empirical[55,87].

The simple and effective "bond order–bond energy" method[88,89] is now widely used for reactions between neutral species because it allows the profiles of reaction paths to be calculated precisely. It is based on empirical relationships between the order and the length of a bond, and between the bond energy D and the bond order n:

$$D = D_S n^p$$

where D_S is the energy of the simple bond and p is an empirical parameter termed the bond index.

The method can be applied to IMR without fundamental changes[90,91], though the bond index for an ion has to be calculated in a different way. In the case of neutral species this index is calculated from the parameters of diatomic complexes of the inert gases, whereas in the case of ions the parameters of "inert gas atom–alkali metal positive ion" complexes have to be used. This method makes some allowance for the specific properties of the bond between an ion and a neutral particle.

The method has been applied to about 20 proton or hydrogen atom transfer reactions of the type of

$$HeH^+ + He \rightarrow He + HeH^+$$
$$H_2^+ + He \rightarrow HeH^+ + H$$
$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \quad .$$

Examples of complex exchange IMR involving the transfer of atoms from the second period of the Periodic Table will be given in the last section of the present review: the path profiles for these reactions were calculated by a modified "bond order–bond energy" method.

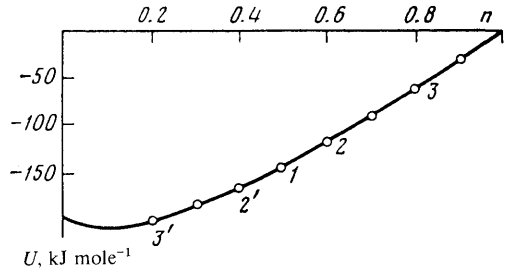


Figure 2. Profile of the reaction path $HeH^+ + Ar \rightarrow He + ArH^+$; U is the potential energy, n is the order of the He–H^+ bond. The distance R between the He and Ar atoms in the linear reactive complex He...H...Ar is 2.52 Å at point *1*, 2.54 Å at points *2* and *2'*, and 2.65 Å at points *3* and *3'*.[128]

The path profile of the reaction

$$HeH^+ + Ar \rightarrow He + ArH^+$$

is shown in Fig.2. Decreasing n from 1 to 1/2 causes a decrease in R due to the closer approach of the reactants, but if n is decreased still further the repulsion of the products causes R to increase. The energy of reaction is released mainly during the approach of the reactants. According to the Eyring–Polanyi rule in this case most of the reacton energy is localised in the vibrational degrees of freedom of the product (ArH^+). When $R \cong 2.8$ Å we find a small minimum in the potential energy, indicating the possibility of stable existence of the $[ArHHe]^+$ ion, with a dissociation energy of ~1.0 kcal $mole^{-1}$. There is no potential barrier in the reaction profile. These results (absence of activation energy and preferential evolution of the reaction energy in a vibrational form) are typical of all the proton transfer reactions so far examined.

In the case of the hydrogen atom transfer reaction

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \qquad (14)$$

the bond index was calculated by making the potential barrier in the path profile of the reaction equal to the experimentally measured activation energy. The barrier for this reaction was found to be displaced towards the reactants, showing that in this case the barrier is most effectively surmounted by the translational energy of the reactants.

The dependence of the cross-section of the reaction

$$NH_3^+ + D_2 \rightarrow NH_3D^+ + D \qquad (15)$$

on the translational energy of the ion and on the energy of its vibrational excitation has been studied experimentally[92], using a double mass spectrometer with coaxial primary and secondary ion beams[93]. The influence of vibrational excitation on the cross-section of the IMR (15) has been studied experimentally on a photo-ionisation mass spectrometer[22].

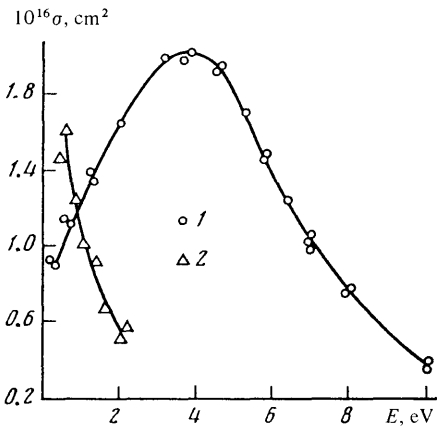


Figure 3. Cross-sections of the reactions $NH_3^+ + D_2 \rightarrow NH_3D^+ + D$ [92] (*1*) and $D_2^+ + H_2 \rightarrow D_2H^+ + H$ [94] (*2*) as a function of the relative kinetic energy of the reactants (the scale of curve *2* is a factor of 10 smaller).

The dependence of the reaction cross-section σ on the kinetic energy E_k of the NH_3^+ ions (assumed to be localised at the centre of gravity of the ion) is shown in Fig.3. When the energy is increased to ~4 eV the cross-section increases to 2×10^{-16} cm^2, but it begins to decrease if E_k is increased still further. This shows that the translational energy of the relative motion of the reacting species is effective in activating the reaction, in keeping with the theoretical calculation of the profile of the reaction path[91]. For comparison Fig.3 also shows the dependence[94] of σ upon E_k for the reaction

$$D_2^+ + H_2 \rightarrow D_2H^+ + H$$

which is typical of an exothermic reaction without activation energy.

The dependence of the cross-section of reaction (15) and of the reaction

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2 \qquad (16)$$

on the ionising photon energy (Fig.4) shows the effect of the vibrational excitation of the electronic ground state of the primary ions formed by electron removal from a non-bonding nitrogen orbital on the yield of secondary ions. An increase in photon energy raises the vibrational excitation energy of the NH_3^+ ions to ~1 eV. Under these conditions the cross-section of reaction (16) decreases slightly, according to Potapov[21], as expected for a fast exothermic reaction. The increase in the cross-section of reaction (15) with the vibrational excitation energy of the NH_3^+ ions shows that the vibrational energy of the ion plays an important part in surmounting the activation barrier of the IMR: in other words, it is incorrect to consider the kinematics of the reactants in reaction (15) merely in terms of a simpler linear model with a two-dimensional potential energy surface[91].

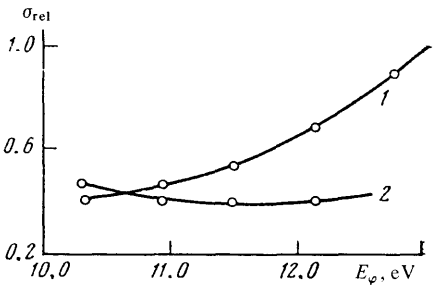


Figure 4. Dependence of the relative cross-sections of the reactions $NH_3^+ + D_2 \rightarrow NH_3D^+ + D$ (*1*) and $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ (*2*) on the photo-ionisation energy E_ϕ. [92]

The dependence of the IMR cross-section on the excitation energy of the ion has been studied in detail by the photoelectron–photo-ion coincidence method[25], but so far only for reaction (4). The results (Fig.5) for different kinetic energies of the relative motion of the reactants give a $\sigma(E)$ relationship consistent with the prediction from statistical theory: the cross-sections decrease as the excitation energy of the reactants increases, and the effect is most marked at the lower translational energies[62]. The application of the statistical theory is not entirely justified in this case, because molecular beam experiments have shown that even at low translational energies the life-time of the intermediate complex is less than the rotation period of the complex, i.e. the reaction takes place by a direct mechanism. The absence of a long-lived complex in reaction (4) has been confirmed by calculations[96] of the potential energy surface for H_4^+.

In addition to reaction (15), the following exothermic reactions have been shown[97] to be slow:

$$CH_3OH^+ + D_2 \rightarrow CH_3OHD^+ + D \ , \qquad (17)$$

$$C_2H_5OH^+ + D_2 \rightarrow C_2H_5OHD^+ + D \ , \qquad (18)$$

$$C_2H_5OH^+ + CD_4 \rightarrow C_2H_5OHD^+ + CD_3 \ , \qquad (19)$$

$$CH_3NH_2^+ + D_2 \rightarrow CH_3NH_2D + D \ , \qquad (20)$$

$$CH_3NH_2^+ + CD_4 \rightarrow CH_3NH_2D^+ + CD_3 \ . \qquad (21)$$

A possible explanation of the anomalous behaviour of the IMR (17)–(21) is suggested in Ref. 97. In all these reactions the recombination energy of the reactant ions is very different from the ionisation potential of the reactant molecules: the recombination energies of the NH_3^+, CH_3OH^+, $C_2H_5OH^+$, and $CH_3NH_2^+$ ions are 10.1, 10.8, 10.5, and 9 eV respectively, whereas the ionisation potential of H_2 is 15 eV. The molecular orbital diagram for the participants in these reactions is shown in Fig. 6*a*. The upper, half-filled orbital of the reacting ion A^+ lies at a large distance from both the occupied and the unoccupied orbital of D_2.

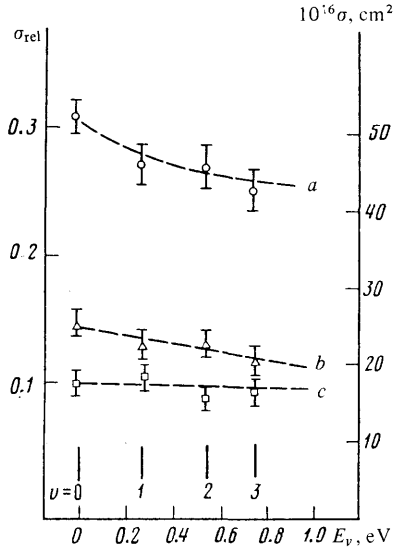


Figure 5. Cross-section of the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ as a function of the vibrational excitation energy of the H_2^+ ion for different energies of the relative motion of the reactants [25]: *a*) 0.11, *b*) 0.46, *c*) 0.93 eV; σ_{rel} [defined as $I_{H_3^+}/(I_{H_3^+} + I_{H_2^+})$] is the ratio of the H_3^+ and H_2^+ ion currents, E_v is the vibrational excitation energy, v is the vibrational quantum number.

According to perturbation theory[98–100] the attractive energy between particles at distances consistent with chemical re-grouping is inversely proportional to the difference in energy between the interacting orbitals. For example, in the simplest two-electron system the interaction between He^+ and H (which have very different orbital energies) leads to a net repulsion both in the $^3\Sigma$ and in the $^1\Sigma$ state[100]. In addition to the interaction of the lower unoccupied orbital of D_2 with the upper half-filled orbital of the A^+ ion, which can only cause weak attraction, we must also consider the interaction of the occupied D_2 orbital with the occupied A^+ orbital, which have similar energies. This interaction between occupied orbitals can lead to repulsion (similar to the repulsion between atoms with full electron shells). The overall effect of the interaction between these pairs of orbitals could be to create an energy barrier opposing the reaction. Reaction (16), like reaction (15), has a high rate constant[17] (10^{-9} cm^3 s^{-1}), typical of an exothermic IMR. This can be explained by the similarity of the energies for the upper molecular orbitals of the reactants NH_3^+ and NH_3, which leads to a net attraction, similar to the attraction observed in simpler systems with equal molecular orbital energies (H^+...H, H...H, He^+...He).

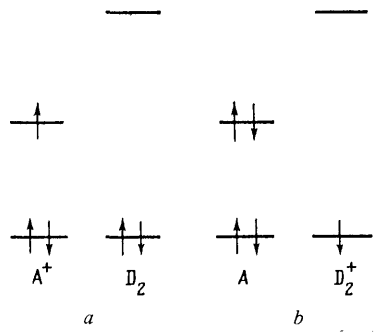


Figure 6. Molecular energy level diagram for the $A^+ + D_2$ (*a*) and $A + D_2^+$ systems (*b*).[97]

We shall now examine the reaction

$$NH_3^+ + CD_4 \rightarrow NH_3D^+ + CD_3 \cdot \qquad (22)$$

The upper energy level diagram for the reactants is qualitatively similar to the diagram of Fig. 6*a*, but the ionisation potential of CD_4 is 2.7 eV lower than the ionisation potential of H_2, and therefore the distance between the occupied upper orbitals of NH_3^+ and CD_4 is less than the corresponding distance for NH_3^+ and H_2. This is a case intermediate between reactions (15) and (16), and the attraction between the reactants NH_3^+ and CD_4 should be greater than the attraction between NH_3^+ and D_2. The methanol ion CH_3OH^+ also reacts more rapidly with CD_4 than with D_2. The rate constants of the reaction of the ethanol ion $C_2H_5OH^+$ with CD_4 and with D_2 are both small. Since the ionisation potential of alcohols decreases as the length of their hydrocarbon chain increases, the above considerations suggest that the molecular ions of all the $C_nH_{2n+1}OH^+$ alcohols with $n > 1$ should react very slowly with molecular hydrogen and deuterium.

Let us now consider the reaction

$$H_2^+ + NH_3 \rightarrow NH_4^+ + H \qquad (23)$$

analogous to (15) but with the opposite localisation of charge on the reactants. The configuration and occupancy of the energy levels of the reactants are similar to those shown in Fig. 6*b*. In this case the interaction between the half-filled orbital of H_2^+ and the inner filled orbital of A, which has a very similar energy, produces an attractive force between the particles at small distances. The rate constant of reaction (23) and that of the corresponding reaction involving D are high (10^{-9}–10^{-10} cm^3 s^{-1}),[17] as expected from the attraction between the reactants. We note that reaction (23) (like the analogous reaction with D_2^+) is strongly exothermic, and therefore the secondary ion can dissociate, with formation of NH_3^+ and NH_2^+ (or NH_2D^+ and NHD^+). Furthermore, the interaction between an ion with a high recombination energy and a complex molecule with a relatively low ionisation energy is usually accompanied by charge transfer[102], because of the ease with which resonance transitions can take

place in the closed-spaced system of energy levels of the complex molecule. Charge transfer by resonance process can take place at much greater distances than the transfer of heavy particles. This makes the rate constant of a reaction involving the transfer of a heavy particle lower than in the absence of competing charge transfer processes[103]. The competition between the charge transfer reaction

$$Ar^+ + CH_4 \rightarrow Ar + CH_3^+ + H$$

and the hydrogen atom transfer reaction

$$Ar^+ + CH_4 \rightarrow ArH^+ + CH_3 \qquad (24)$$

can account for the presence of an energy threshold[104] in the exothermic reaction (24). At low kinetic energies the charge transfer and the subsequent fast dissociation of the excited ion

$$(CH_4^+)^* \rightarrow CH_3^+ + H$$

take place while the reacting particles are relatively far apart, and the closer approach of Ar and CH_3^+ cannot lead to a re-grouping of the heavy particles because this process would be endothermic. As the kinetic energy of the reactants increases, the time during which they are in contact after the redistribution of charge becomes comparable to the dissociation time of the excited molecular ion, and the effectiveness of reaction (24) (with a re-grouping of heavy particles) increases.

A similar explanation can be suggested for the appearance of a potential barrier[105] in the reaction

$$N_2^+ + CH_4 \rightarrow N_2H^+ + CH_3 .$$

Other reactions between ions with a high recombination energy and complex molecules with a relatively low recombination coefficient can be expected to be slow, for the same reason: for example

$$Ar^+(N_2^+, H_2^+) + C_nH_{2n+2} \rightarrow ArH^+(N_2H^+, H_3^+) + C_2H_{2n+1} .$$

Exothermic reactions between an ion with a high recombination energy and simple molecules with a relatively low ionisation potential and a low density of energy levels may have low rate constants both for the charge rearrangement and for the transfer of heavy particles. A good example is the low efficiency of the reactions between ions with a high recombination energy (He^+ and Ne^+) and the simplest molecule (H_2).[106]

It has been assumed[107,108] that in collisions between particles with a low kinetic energy the electron, ion, and atom transfer processes are fully analogous and controlled by the "random resonance" condition $\tau_t \cong \tau_c$, where $\tau_t = h/|\Delta E|$ is the time of the transition between the electronic-vibrational-rotational energy levels of the reactants and the products separated by a distance ΔE (the energy defect), and $\tau_c = a/v$ is the collision time (a being the effective width of the collision region and v the relative velocity of the translational motion of the reactants). The reaction cross-sections were calculated by the semi-empirical formula

$$\sigma = \begin{cases} \sigma_m \exp\left[k'\left(1 - \frac{a|\Delta E|}{hv}\right)\right] & \text{for } v < \frac{a|\Delta E|}{h} \\ \sigma_m & \text{for } v \geqslant \frac{a|\Delta E|}{h} \end{cases} .$$

Here σ_m is the cross-section of the resonance process for $v = a|\Delta E|/h$, and k' is a parameter whose optimum value is 2. The optimum value of a for IMR is 100 Å. A large value of a corresponds to a spiral trajectory for the motion of the reactants at low kinetic energies. At thermal energies the rate constants were calculated by the formula

$$k = \sigma v .$$

The six lowest possible exothermic energy defects were determined, a cross-section was calculated for each of them, and the results were combined. The calculation included averaging over the rotational states and summing over the accessible electronic levels of the products.

The rate constants of approximately 20 charge transfer and exchange reactions during collisions between mono-atomic and diatomic particles have been calculated. For example, for the reaction

$$N^+(^3P_{0,2,1}) + O_2 \rightarrow NO^+(X^1\Sigma^+, a^3\Sigma^+) + O(^3P_2, {}^1D_2, {}^1S_0)$$

the calculated rate constant is $\sim 3 \times 10^{-10}$ cm^3 s^{-1}, and the experimental value is $\sim 4 \times 10^{-10}$ cm^3 s^{-1}. For the reaction

$$O^+(^4S_{3/2}) + N_2(^1\Sigma_g^+) \rightarrow NO^+(X^1\Sigma^+) + N(^4S_{3/2}) \qquad (25)$$

the calculated rate constant is $\sim 10^{-12}$ cm^3 s^{-1}, and the experimental values lie in the range $(1-3) \times 10^{-14}$ cm^3 s^{-1}. The agreement between calculation and experiment is always good, in spite of the fact that the energy defects are calculated for the isolated reactants and no allowance is made for the effect of Franck–Condon factors in the transition probabilities.

Though the calculations are simple (in principle), they require a knowledge of the energy levels, and therefore they rely on accurate spectroscopic data, which are not always available. We should also note that calculations by this method predict a positive temperature effect for slow IMR, whereas reactions such as (25) show a negative temperature effect at low kinetic energies.

V. LAW OF CORRELATION OF THE SYMMETRY OF STATES

A qualitative method of estimating the rates of chemical reactions is implicit in the law of conservation of state symmetry in reactions. Reactions are considered to be allowed if the symmetries of the wave functions and the total spin of the electronic ground state are the same for reactants and products. In reactions between an atom and a diatomic molecule or between two diatomic molecules under conditions leading to the formation of linear product molecules the symmetry type of the reactants and products is determined by the quantum number of the orbital angular momentum. In this case conservation of symmetry reduces to conservation of the resulting angular momentum of reactants and products.

Reactions which are forbidden in this sense can take place only if the reactants or the products are electronically excited.

The law of conservation of state symmetry has been used to explain[109] the anomalously low rate constant of the ion-molecule reaction (25), which is important in the chemistry of the Earth's ionosphere. It was pointed out[110] that under laboratory conditions and for a kinetic energy of the O^+ ion of a fraction of an electron-volt the rate constant of this reaction is $\sim 10^{-11}$ cm^3 s^{-1}, which is much lower than the Langevin limit. Reaction (25) was later studied in detail by different methods and over a wide range of kinetic energies of the ions (Fig.7). Measurements in a drift tube at kinetic energies of 0.04–2 eV detected an initial decrease in the reaction cross-section, with a minimum of ~ 0.01 Å^2 at an energy of 0.3 eV, followed by an increase in cross-section with ion energy. In the high energy region the measurements were made with a double mass spectrometer. The highest cross-section (~ 5 Å^2) is reached for a kinetic energy of 8 eV, and beyond this point the cross-section falls off very steeply.

The ground states of the reactants are $^1\Sigma_g^+$ for N_2 and ^4S_u for O^+. The linear approach of N_2 and O^+ gives N_2O^+ in the $^4\Sigma^-$ excited state. Without allowance for the polarisation energy the potential energy curve for this state has no

minimum, and the energy increases monotonically as the particles move closer together. The potential curve for the reaction products $NO^+(^1\Sigma^+)$ and $N(^4S_u)$ has a similar shape. The potential surface calculated for $N_2O^+(^4\Sigma)$ has a potential barrier between the reactants and products of this exothermic IMR ~8 eV high, and the depth of the potential well due to the polarisation attraction between the reactants[111] is ~0.38 eV. Since the two branches of the energy curve for the $^4\Sigma^-$ state intersect the potential curve of the ion in the ground state $[N_2O^+(^2\Pi)]$ the reaction can follow a different path which avoids the high potential barrier. The low probability of reaction (25) at low kinetic energies can be ascribed to the low probability of non-adiabatic transitions from the $^4\Sigma^-$ curve (corresponding to the approach of the O^+ ion towards the N_2 molecule) to the curve for the ground state of $N_2O^+(^2\Pi)$, and of the backward transitions from the $N_2O^+(^2\Pi)$ curve to the $^4\Sigma^-$ curve, corresponding to the separation of the NO^+ and N products, since these transitions are forbidden for orbital angular momentum and for spin.

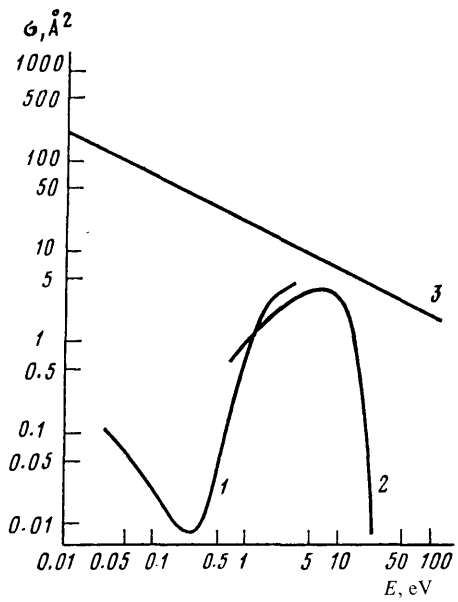


Figure 7. Cross-section of the reaction $O^+ + N_2 \rightarrow NO^+ + N$ against the kinetic energy of the O^+ ion. Cross-sections measured: *1*) by the drift tube method[18] and *2*) by using a double mass spectrometer[118]. Curve *3* denotes the cross-section of the ion–molecule collisions, calculated by formula (2).

The increase in reaction cross-section with kinetic energy of the ions arises from the increased probability of non adiabatic transitions, whereas the decrease in cross-section in the low-energy region can be explained by the decrease in life-time of the soft polarisation complex[112]. We note that the activated complex theory as used to explain the negative temperature dependence of the IMR rate in the case of the transfer of a hydride ion can also explain the change in sign of the effect of ion energy on the rate constant (because of the increased contribution from the vibrational partition functions when the complex has a high energy[113]).

The decreasing cross-section of reaction (25) at high ion energies has been explained[114] by the direct reaction mechanism (removal of a nitrogen atom followed by capture of the incident O^+ ion with formation of the molecular ion NO^+). The theory of these reactions[115] assumes that the system of particles remains on a fixed energy surface throughout the reaction, that the interaction potential V is of the pair type, and that the interaction between the ion and the bound nitrogen atom can be treated in the impulse approximation, i.e. that we can write

$$\omega a/v \ll 1$$

where ω is the vibrational frequency of the molecule. The calculated dependence of the cross-section on the ion energy correctly reflects the most striking feature of the experimental curve: a steep fall of σ with increasing energy of the colliding particles for $E > 12$ eV. The position and height of the maxima in the theoretical and the experimental curve are almost the same, and the position of the maximum in the theoretical curve corresponds to the largest phase volume defined by the capture conditions. Thus the complex energy dependence of the cross-section of reaction (25) is adequately explained by existing qualitative models.

The law of conservation of orbital momentum can also explain the difference between the rate constants of the isotope exchange reactions

$$^{15}N^+ + {}^{14}N_2 \rightarrow {}^{14}N^+ + {}^{14}N^{15}N \quad , \qquad (26)$$

$$^{18}O^+ + {}^{16}O_2 \rightarrow {}^{16}O^+ + {}^{16}O^{18}O \quad . \qquad (27)$$

The rate constant of reaction (26) is more than two orders of magnitude greater than that of reaction (27): this has been ascribed[116] to the symmetry- and spin-forbidden formation of a triatomic linear complex in the electronic ground state in the case of reaction (27) but not of reaction (26). It has been shown[117] that exothermic IMR with proton transfer of the type of

$$C^-(^4S) + XH \rightarrow X^- + CH(^2\Pi)$$

(where X is a radical of various types) are usually slow, but they become fast when the energy evolved by the reaction is sufficient to give $CH(^4\Sigma)$ as a product.

Some reactions involving relatively simple molecules are incompatible with the above law. For example, though the reaction

$$N^+(^3P) + O_2(^3\Sigma) \rightarrow NO_2^+(^1\Sigma) \rightarrow NO^+(^1\Sigma) + O(^3P) \qquad (28)$$

is forbidden for orbital angular momentum conservation, and the reaction

$$O^+(^4S) + CO_2(^1\Sigma) \rightarrow O_2^+(^2\Pi) + CO(^1\Sigma) \qquad (29)$$

is also spin-forbidden, their rate constants are close to the Langevin limit (5×10^{-10} and 11×10^{-10} $cm^3\ s^{-1}$ respectively[118]).

The removal of the restrictions on reaction (28) is due to the strong coupling between the rotational and the orbital momentum of the electron[119], and in the case of reaction (29) it is due to the strong coupling between the orbital and the spin momentum. The spin-orbital coupling in the intermediate complex of reaction (29) has been shown[119] to be due to the strong resonance interaction of the reactants, arising from the very similar values of the ionisation potential in O and CO_2.

Cases of symmetry-allowed yet slow reactions have also been reported. For example, the exothermic exchange reaction

$$CO^+(^2\Sigma^+) + O_2(^3\Sigma_g^-) = CO_2^+(^2\Pi_g) + O(^3P) \qquad (30)$$

is slow, whereas the competing (forbidden) exothermic charge transfer reaction

$$CO^+(^2\Sigma^+) + O_2(^3\Sigma_g^-) \rightarrow CO(^1\Sigma^+) + O_2^+(^2\Pi) \quad (31)$$

is fast[120].

We note that a theoretical explanation of the high rate of reactions (28) and (29) can be put forward. In the case of IMR of the type of

$$A^{\pm} + BC \rightarrow AB^{\pm} + C \quad (32)$$

(where A, B, and C can be carbon, oxygen, and nitrogen atoms) a simple method of calculating the rate constant can be based[121] on the assumption that the reaction will be fast if it does not involve a substantial redistribution of the charge density. This hypothesis leads to the rule that reaction (32) will have a large cross-section if atom A is less electronegative than atom B (in the case of IMR involving positive ions), since the positive charge in the reaction product AB^+ can then remain on the atom A.

In the case of reactions involving negative ions we can expect a large cross-section if the electronegativity of the A atom is greater than that of the B atom. If the electronegativities of A and B are similar, the reactions in which the redistribution of electron density in the product molecule C as compared with the reactant BC is least marked will be the fastest. This will be the case when the C molecule has the same dipole moment and the same geometry as the BC molecule. It has also been pointed out that the rate constants of slow IMR involving a rearrangement of the electron density increase with the internal energy of the reactants, whereas in fast IMR (with an unchanged electron density) the rate constants decrease as the internal energy increases.

Let us examine the application of the electronegativity rule to reaction (25). The oxygen is more electronegative than the nitrogen atom: we can therefore expect reaction (25) to have a low efficiency. In reaction (29) the CO_2 molecule has no net dipole moment, though the electron density is sharply divided between the oxygen atoms and the carbon: as a result, the oxygen atoms carry a negative charge and the carbon atom a positive charge. In the CO molecule the negative charge is also shifted towards the oxygen, i.e. reaction (29) can take place without a major redistribution in the electron density. According to the rule formulated above we can expect this reaction to be fast.

The rule was later extended[123] to IMR of the type of

$$AH_k^+ + BCH_l \rightarrow ABH_m^+ + CH_n$$
$$AH_k^+ + BH_l \rightarrow ABH_m^+ + p\,H_2 + q\,H$$
$$AH_k^+ + BCH_l \rightarrow ABCH_m^+ + p\,H_2 + q\,H$$

where A, B, and C are large central atoms, and k, l, m, n, p, and q are integers. To a first approximation the hydrogen atoms can be ignored, so that only the electronegativity of the large central atoms needs to be considered. A large number of IMR has been examined[121], and the validity of the rule has been demonstrated. For example, symmetrical exchange reactions with transfer of the electronegative O^+ ion are found to be slow[122,124,125]:

$$^{12}CO_2^+ + {}^{13}CO \rightarrow {}^{12}CO + {}^{13}CO_2^+ , \quad (33)$$

$$^{14}N_2O^+ + {}^{15}N_2 \rightarrow {}^{15}N_2O^+ + {}^{14}N_2 . \quad (34)$$

The slowness of these reactions can also be explained by the need for excitation of the reactants in the intermediate decomposition step of the primary ion, since the ground states of the linear CO_2^+ and N_2O^+ ions do not correlate with the ground states of the decomposition products $CO + O^+$ and $N_2 + O^+$.[124]

The fast IMR

$$C^+ + O_2 \rightarrow O^+ + CO \quad (35)$$

in which charge is transferred from the less electronegative C atom to the more electronegative O^+, is incompatible with the electronegativity rule[126]. The reaction

$$C^+ + O_2 \rightarrow CO^+ + O \quad (36)$$

in which the positive charge remains on the C atom, is slower[126] than reaction (35). In this case the contradiction can be explained by postulating a two-step elementary act: initially the intermediate complex has the structure $[O...CO^+]$, corresponding to the products of reaction (36), but in a time comparable to the dissociation time this complex undergoes an internal charge redistribution and is converted into the more stable $[O^+...CO]$ structure, corresponding to the products of reaction (35).

The following exothermic reactions were found to be slow:

$$N^+(^3P) + CO(^1\Sigma) \rightarrow NO^+(^1\Sigma) + C(^3P) \quad (37)$$

$$N^+(^3P) + CO_2(^1\Sigma_g) \rightarrow NO^+(^1\Sigma) + CO(^1\Sigma) \quad (38)$$

though the positive charge in the NO^+ ion is concentrated on the N atom[127–129]. Reaction (37) is symmetry allowed. It is interesting to note that the reactants in reactions (37) and (38) can undergo the fast non-dissociative charge transfer reactions:

$$N^+ + CO \rightarrow CO^+ + N . \quad (39)$$

$$N^+ + CO_2 \rightarrow CO_2^+ + N . \quad (40)$$

The dependence of the cross-sections of reactions (37) and (39) on the kinetic energy of the ions (E_i) is illustrated in the Table.

Cross-sections of reactions (37) and (39) as a function of the kinetic energy of the ions[128].

E, eV	0.2	0.5	1.0	2.5	5.5	10.0	20.0
σ_{37}, Å^2	2.6	1.3	0.6	0.4	1.0	0.9	0.17
σ_{39}, Å^2	28	10	4.8	2.4	2.0	2.6	3.3

When the kinetic energy is increased from 0.2 to 20 eV the cross-section of the IMR (37) initially decreases from 2.6 to 0.4 Å^2 (at 2.5 eV), then increases to ~1 Å^2 (at 5.5 eV), and finally falls off sharply, reaching 0.17 Å^2 at 20 eV. The cross-section of the charge transfer process (39) initially decreases from 28 to 2 Å^2 (at 5.5 eV), and then increases to 3.3 Å^2 at 20 eV. Thus the allowed reaction (37) has a low cross-section, whose dependence on the kinetic energy of the ion is similar to that of the forbidden reaction (25). The cross-section of reaction (38) at a kinetic energy of 2 eV is only 6% of the cross-section of the charge transfer reaction (40).[129]

The statistical theory, which allows for the formation of only one type of intermediate complex, predicts the opposite ratio of cross-sections for heavy particle transfer and charge transfer reactions, since in the examples considered the enthalpy of the heavy particle transfer reactions is greater than the enthalpy of charge transfer. The observed relative

cross-sections can be explained only if the initially formed soft complex has a short life-time (as a result of a fast exothermic charge rearrangement, which can take place at relatively long distances in a soft complex). This effect inhibits the formation of the hard complex, which must precede the regrouping of the chemical bonds. Thus the non-dissociative charge transfer processes (like the dissociative processes discussed above) can lower the cross-section of IMR involving the regrouping of heavy particles.

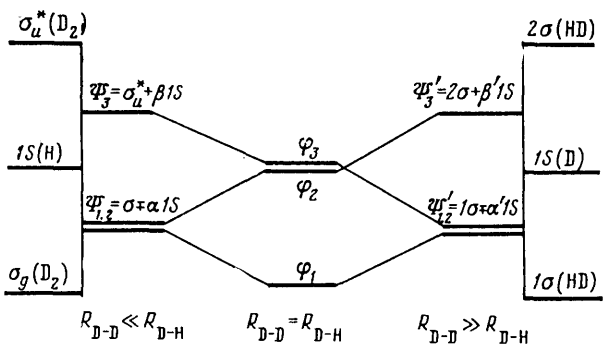


Figure 8. Correlation diagram of the molecular orbitals of the D...D...H system[130].

VI. LAW OF CONSERVATION OF ORBITAL SYMMETRY

The rate constants of IMR can be discussed qualitatively by drawing the correlation diagrams for the molecular orbitals, based on the law of conservation of the symmetry of molecular orbitals during a reaction. For the linear HD_2 system the correlation diagram of the molecular orbitals[130] is shown in Fig.8. The diagram explains the difference in probability of the reactions

$$H^+ + D_2 \rightarrow HD + D^+ \qquad (41)$$

$$H + D_2 \rightarrow HD + D \qquad (42)$$

$$H^- + D_2 \rightarrow HD^- + D \qquad (43)$$

in which the occupancy of the $1S(H)$ orbital is 0, 1, and 2 respectively. It is clear from the diagrams that the $\sigma_g(D_2)$ orbital correlates with the lowest orbital (ϕ_1) of the complex. In the course of the reaction two electrons are transferred from the $\sigma_g(D_2)$ orbital through the ϕ_1 orbital of the intermediate complex to the $1\sigma(HD)$ orbital of the product. For reaction (41), in which only two electrons take part, the close approach of the reactants lowers the potential energy, and should lead to a fast reaction. The electrons located on the $1S(H)$ orbital are transferred to the ϕ_2 orbital of the intermediate complex, which has a node, and therefore the potential energy increases as the reactants move closer together. The greater the number of electrons in the orbital, the stronger the repulsion. Therefore reaction (41) should be fast, and reaction (43) should be the slowest, though attractive polarisation forces between the ion and the molecule are present in both cases. This conclusion has been confirmed experimentally[131,132]. The recently discovered[132] activation energy for the exothermic proton transfer IMR

$$NH_2^- + H_2 \rightarrow H^- + NH_3$$

$$CH_2{=}CH{-}CH_2^- + C_6H_5CH_3 \rightarrow C_6H_5CH_2^- + CH_2{=}CH{-}CH_3$$

probably has a similar origin. Here, as in reaction (43), a negative ion interacts with a molecule which has no partially filled orbitals.

The correlation diagram shown in Fig.8 also explains the low efficiency of IMR of the type of

$$D_2^+ + H \rightarrow DH^+ + D$$

since in this case only one electron is found on the bonding orbital (ϕ_1) of the complex, whereas the second electron is transferred to the antibonding ϕ_2 orbital. Under these conditions the resulting interaction is repulsive, because the increase in energy of the antibonding orbitals caused by bringing the particles closer together is usually much greater than the corresponding decrease in energy of the bonding orbitals. Vibrational excitation of the D_2^+ ion raises the $\sigma_g(D_2)$ level, bringing it closer to the $1S(H)$ level, and thus facilitates electron transfer from the $1S(H)$ to the $\sigma_g(D_2)$ level. This opens a path for charge transfer and new paths for non-adiabatic exchange reactions involving the ground state and the first electronically excited state of the D_2H^+ complex. The calculation of the dependence of the cross-section of non-adiabatic IMR on the kinetic and internal energies of the ions requires a detailed knowledge of the potential energy surfaces of the ground and the excited state of the D_2H^+ system, and of the probabilities of transitions between these states[54,133].

The correlation diagram[106] for the reactions

$$He^+ + H_2 \rightarrow HeH^+ + H \qquad (44)$$

$$H_2^+ + He \rightarrow HeH^+ + H \qquad (45)$$

is similar to the diagram shown in Fig.8, differing from it only in the absence of resonance between the energy levels of reactants and products. In reaction (44) one electron is found on the $1S(He)$ orbital and two on the $\sigma_g(H_2)$ orbital. During the reaction the electron in the $1S(He)$ orbital is adiabatically transferred to the $1\sigma(HeH)$ orbital. The two electrons from the $\sigma_g(H_2)$ orbital are transferred to the antibonding orbital of the complex, from which they pass into the antibonding $2\sigma^*(HeH)$ orbital, giving the highly excited HeH* particle and a proton. Alternatively, the two electrons can be transferred to the $1S(H)$ level in the region of contracting orbital energies, giving HeH^{2+} and H^-. These two reaction channels are allowed for orbital symmetry, but they are strongly endothermic and therefore inaccessible at low kinetic energies. The exothermic channel giving $HeH^+ + H$ from the reactants He^+ and H_2 is forbidden, because it requires the transfer of an electron between potential surfaces of very different energy which nowhere approach each other sufficiently closely. A similar set of arguments shows that all reactions of the type of

$$He^+(Ne^+) + XH \rightarrow HeH^+(NeH^+) + X$$

must be slow (X is a radical with an ionisation potential a few eV lower than the ionisation potential of Ne).

In reaction (45) the $1S(He)$ orbital is occupied by two electrons, and the $\sigma_g(H_2)$ orbital by one electron. In this case the molecular orbitals of the ground states of reactants and products are correlated, and reaction (45) can be expected to be fast (as is found experimentally[106]). A reaction is facile when the orbitals of the reactants in their ground state

are correlated to those of the products in their ground state. If on the other hand the ground state orbitals are correlated to those of an excited state we can expect the reaction to be very ineffective (at low kinetic energies and low internal excitation energies) towards endothermic processes with formation of excited products.

The correlation diagrams for a large number of IMR involving complex atoms are given in Ref.106. Forbidden reactions include double decompositions by a planar four-centre cyclic transition state[134], such as

$$H_2 + D_2 \rightarrow 2HD \ . \qquad (46)$$

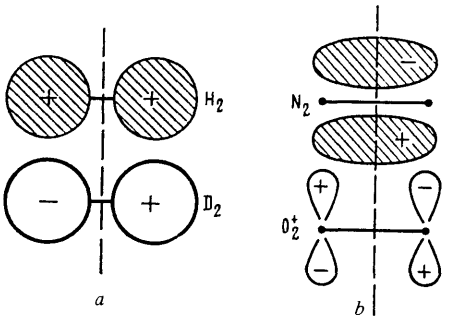


Figure 9. Molecular orbitals involved in the reactions $H_2 + D_2 \rightarrow 2HD$ (*a*) and $O_2^+ + N_2 \rightarrow NO^+ + NO$ (*b*).

In the case of the reaction

$$AB + CD \rightarrow AD + BC \qquad (47)$$

and assuming that the orbital energies are equal to the corresponding bond energies of the molecules, the correlation diagrams give the following expression for the activation energy[135]:

$$E_a = \frac{D(CD)\,[D(CD) + D(AB) + D(AD) - D(BC)]}{D(CD) + D(AD)} \qquad (48)$$

where D(AB) and D(CD) are the dissociation energies of the stronger and the weaker bond in the reactants, and D(AD) and D(BC) are the dissociation energies of the weaker and the stronger bond in the products. For example, for reaction (46) the activation energy calculated by this formula is 420 kJ mole^{-1}. In the case of molecules consisting of atoms with many electrons the orbital correlation diagrams become extremely complex, and in order to classify a reaction as forbidden or allowed we must use Pearson's method[136,137], in which only the highest occupied and the lowest unoccupied orbitals of the reactants are considered. Whereas in the Woodward and Hoffman method[134] the correlation between the molecular orbitals of reactants and products in their ground states is used as a criterion of whether the reaction is allowed or forbidden, in the Pearson approach the criterion is the positive overlapping of the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. For the chemical reaction to have a low activation energy we require the HOMO of the donor to have the same symmetry as the LUMO of the acceptor, and the transfer of an electron from the donor to the acceptor must weaken the bonds being broken and strengthen those being created. In reactions involving positive ions the donor is always the reactant molecule, and in reactions with negative ions the molecule is always the acceptor.

The shape of the molecular orbitals taking part in reaction (46) is shown in Fig.9*a*. The occupied bonding orbital of H_2 is cross-hatched, and the unoccupied D_2 antibonding orbital is left blank. These orbitals have different symmetries, and the approach of the reactants leads to repulsion (and hence to a high activation energy for the reaction).

In the isotope exchange reactions

$$^{15}N_2^+ + {}^{14}N_2 \rightarrow {}^{15}N^{14}N^+ + {}^{15}N^{14}N$$
$$^{18}O_2^- + {}^{16}O_2 \rightarrow {}^{18}O^{16}O^- + {}^{18}O^{16}O$$

electrons are transferred from an N_2 bonding orbital to an N_2^+ bonding orbital, and from an O_2^- antibonding orbital to an O_2 antibonding orbital. The overlap of the orbitals is positive in both cases (the overlapping orbitals have the same sign), but the electron transfer weakens one of the existing bonds and strengthens the other. Therefore these reactions also are forbidden.

Another example of the application of Pearson's rule to IMR is the double decomposition reaction

$$N_2^+ + O_2 \rightarrow NO^+ + NO \qquad (49)$$

which has a very small cross-section[138]. In this case the acceptor is the N_2^+ ion, whose lowest unoccupied orbital is the $\sigma_g(2p_x)$ bonding orbital. The highest occupied orbital of O_2 is the antibonding π_g^x orbital. Again, the orbitals of the reactants have different symmetries with respect to the plane normal to the axis of the molecule, and this accounts for the slowness of the reaction.

A reaction analogous to (49) but with the opposite charge distribution on the reactants

$$O_2^+ + N_2 \rightarrow NO^+ + NO \qquad (50)$$

is also forbidden, since in this case the electron has to be transferred from a bonding N_2 orbital to an antibonding O_2^+ orbital (Fig.9*b*).

An experimental study[139] of ion-molecule reactions caused by collisions between O_2^+ and N_2 has shown that if the kinetic energy of the O_2^+ ions is less than 15 eV the rate constant of the formation of NO^+ is less than 3×10^{-13} cm^3 s^{-1}. Under these conditions NO^+ can be formed by the reaction

$$O_2^+ + N_2 \rightarrow NO^+ + N + O \qquad (51)$$

as well as by reaction (50). It has also been reported[138] that the weakly endothermic reactions [analogous to (51)]

$$NF^+ + O_2 \rightarrow NO^+ + F + O \qquad (52)$$

$$N_2^+ + O_2 \rightarrow NO^+ + N + O \qquad (53)$$

have very small cross-sections (less than 10^{-17} cm^2 for ions with kinetic energies between 2 and 50 eV), whereas the cross-sections of the strongly endothermic dissociations

$$NF^+ + O_2 \rightarrow N^+ + F + O_2$$
$$N_2^+ + O_2 \rightarrow N^+ + N + O_2$$

are much higher.

The most likely reason for the lack of dependence of the rate of exchange reactions on the kinetic energy of the reactants is a displacement of the potential barrier towards the products for reactions (51)–(53) or towards the high-curvature region of the path for reactions (49) and (50). The profiles of the reaction paths for some symmetry-forbidden double decomposition reactions of the type of (50) and of exchange reactions with dissociation of the type of (51) have recently been calculated by a modified "bond order–bond energy" method[140,141].

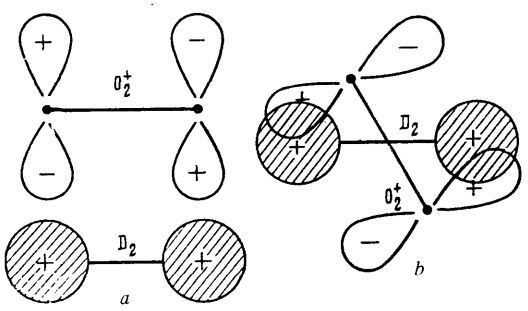


Figure 10. Molecular orbitals participating in the reaction $O_2^+ + D_2 \rightarrow OD^+ + OD$: *a*) is the planar complex, *b*) is a complex formed by the approach of the reactants in a non-parallel mutual configuration.

The approach of the reactants with formation of a non-planar complex can convert a reaction which is forbidden for a planar complex into an allowed reaction. For the reaction

$$O_2^+ + D_2 \rightarrow OD^+ + OD \cdot \qquad (54)$$

the planar complex is shown in Fig.10*a* and the complex formed when the reactants approach each other along an axis perpendicular to the plane of the paper (with the molecular axes in a non-parallel configuration) is shown in Fig.10*b*. In the latter case reaction (58) is allowed, because the overlap of the orbitals is positive and the bond in the reactants is weakened by the electron transfer. The analogous reaction

$$D_2^+ + O_2 \rightarrow OD^+ + OD$$

is forbidden, because the bond in the reactants is strengthened by the electron transfer. These conclusions are consistent with experimental results[138]: the cross-section for the formation of OD^+ is higher for collisions between O_2^+ and D_2 than for collisions between D_2^+ and O_2.

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The examples discussed in this review show the importance of wide-ranging and detailed studies of the elementary reaction act in IMR in establishing the origin of the chemical reactivity and the mechanism of the elementary reaction acts in the chemical regrouping of particles, and in characterising the elementary acts of the energy redistribution processes.

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Heteropolyacids in Catalysis

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The application of heteropolyacids (HPA) as catalysts of oxidation and acid-type reactions as well as certain physicochemical properties of the HPA important for the understanding of the mechanism of their catalytic action are examined. The mechanisms of catalytic reactions in the presence of HPA are discussed.
The bibliography includes 182 references.

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I. INTRODUCTION

The application of heteropolyacids (HPA) as catalysts may be regarded as a new field in catalysis. Systematic study of this field began approximately 10 years ago, although isolated (and frequently successful) attempts to employ HPA in homogeneous and heterogeneous catalytic reactions were made even earlier. Extensive investigation of homogeneous systems based on HPA began after the discovery of the ability of molybdovanadophosphoric acids having the composition $H_{3+n}PMo^{VI}_{12-n}V_nO_{40}$ (HPA-n, where $n = 2-8$) and their salts to undergo reversible oxidation-reduction reactions in aqueous solution[1,2]:

$$\text{HPA-}n + \text{Red} + i\,\text{H}^+ \rightarrow \text{H}_i\text{HPA-}n + \text{Ox}, \quad (1)$$

$$\text{H}_i\text{HPA-}n + (i/4)\text{O}_2 \rightarrow \text{HPA-}n + (i/2)\text{H}_2\text{O}, \quad (2)$$

where Red and Ox are the i-electron reductant (the substrate or the reduced form of the cocatalyst) and its oxidised form respectively and $H_iHPA\text{-}n = H_i[H_{3+n}PMo^{VI}_{12-n}V^{V}_{n-i}V^{IV}_{i}O_{40}]$ is the heteropolyblue—the reduced form of HPA-n ($i \leq n$). The reversibility of the oxidation-reduction properties made it possible to carry out numerous oxidation reactions using HPA-n solutions as catalysts and O_2 as the oxidant[2].

Heteropolyacids have a unique set of valuable catalytic properties. They consist of polynuclear molybdenum(VI), tungsten(VI), and vanadium(V) complexes, which may also include many other elements as central atoms or ligands. HPA are many-electron oxidants and at the same time are strong Brønsted acids. The oxidation-reduction and acid properties of HPA can be varied within fairly wide limits by altering their composition. Many HPA are fairly soluble and stable in water and oxygen-containing organic solvents. At the same time they exhibit a high thermal stability in the solid state. This makes it possible to use HPA as homogeneous and heterogeneous catalysts of oxidation and acid-type reactions and also as bifunctional catalysts.

Among different HPA, the acids and their salts belonging to the saturated 12-series are of greatest importance for catalysis. They include the heteropolyanions (HPA) $X^{x}M^{VI}_{12}O^{x-8}_{40}$ or $X^{x}M^{VI}_{12-n}V^{V}_{n}O^{x-8-n}_{40}$, where X is the central atom (Si^{IV}, Ge^{IV}, P^{V}, As^{V}, etc.), x the degree of oxidation, and M the metal ion (Mo^{VI} and W^{VI}). The representatives of the 12-series are distinguished by a high stability and their properties have been investigated in detail. In this review the HPA are understood as derivatives of the 12-series unless otherwise stated. In the formulae of the HPA the H and O atoms may be omitted for brevity.

Until recently the number of studies devoted directly to the catalytic properties of HPA was less than 1% of the total number of studies on such compounds[3]. In recent years the relative contribution of these investigations increased greatly both in the USSR[2,4] and abroad[5]. This occurred as a result of the synthesis of a large number of new HPA and the accumulation of extensive information about their properties. The main contribution to the development of the chemistry of HPA was made by the schools of Spitsyn and Alimarin in the USSR, Souchay in France, and Pope in the USA.

This review deals with the results of studies on homogeneous and heterogeneous catalytic systems based on HPA carried out mainly during the last 10 years. The physicochemical properties of HPA (mainly in solutions), necessary for the understanding of the mechanism of their catalytic action, are also considered. Several short reviews devoted to the catalytic properties of HPA in homogeneous[1,2,6] and heterogeneous[7] reactions† were published previously. The synthesis, properties, and other applications of HPA of different series were examined in earlier reviews[8-14] and monographs[15,16] and the application of HPA in chemical analysis has been dealt with in two communications[17,18]. One should note that the catalytic properties of HPA are employed in a series of kinetic analytical methods (analyses for phosphorus[19] and arsenic[20]).

II. CERTAIN PHYSICOCHEMICAL PROPERTIES OF HETEROPOLYACIDS

1. The Molecular Structure of HPA of the 12-Series

Molecules of the 12-series HPA of the type $H_{8-x}X^{x}M^{VI}_{12}O_{40}$ and $H_{8-x+n}X^{x}M^{VI}_{12-n}V^{V}_{n}O_{40}$ have the Keggin structure with T_d symmetry (Fig.1), which has been established reliably as a result of numerous X-ray diffraction investigations of HPA hydrates[8-10,21-23]. This structure includes a central XO_4 tetrahedron surrounded by 12 MO_6 octahedra having common edges and vertices (O atoms). It has been frequently suggested that the MO_6 octahedra constitute a single polydentate ligand[9], but the equilibria in the degradative dissociation of HPA in solutions (see below) show that this review is not entirely justified. The radius of the HPA molecule is ~6 Å.[9] Since the ionic radius of O^{2-} greatly exceeds the radii of M^{VI} and X^{x}, the state of the O atoms in HPA is nearly close-packed[10]. The following types of chemical bonds are present in the HPA molecule: 12 quasi-linear bonds, 12 M—O—M angular bonds, 4 X—O—M bonds with bridging O atoms, and 12 M=O bonds with terminal O atoms.

†See also the review by M.Otake, J.Synth.Org.Chem. Japan, 1981, **39**, 385.

In these bonds the coordination numbers of the oxygen atom are 2,2,4 and 1 respectively. Thus the HPA contain the fundamental elements of the structures of the molybdenum, tungsten, and vanadium oxides. The HPA crystallise in the form of hydrates containing variable numbers of molecules of water of crystallisation (up to 30 and more).

2. The State of HPA in Solution. Kinetics and Mechanism of Ligand Substitution

The Keggin structure is preserved in concentrated HPA solutions but in dilute solutions ($<10^{-2}$ M) account must be taken of the degradative dissociation with ligand elimination. The retention of the Keggin structure in concentrated solutions has been demonstrated by X-ray diffraction[24-26] and by the identity of the infrared and Raman spectra of the crystals and aqueous and non-aqueous solutions of the HPA[27-31]. This is also indicated by ^{17}O NMR spectra[32-34] and the results of studies by other physical methods[35].

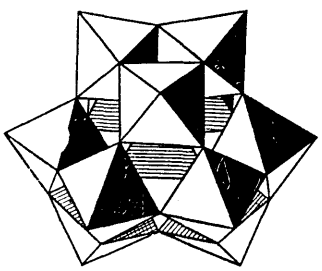


Figure 1. The Keggin structure of the 12-series HPA.[9]

By virtue of the symmetry of the anion and its large size combined with a low surface density of the negative charge, HPA and many of their salts are frequently fully dissociated in solution and the heteropolyanions are weakly solvated and behave as weak complex-forming ligands. The latter does not apply to defective heteropolyanions (HPAn), for example $SiW_{11}O_{39}^{8-}$, in which the vacancy in the Keggin structure has a high coordinating capacity[9,36,37]. The above property of the defective HPA is widely used to obtain HPA with different metal ions in the coordination sphere, for example compounds with polyanions having the general formula $XZW_{11}O_{39}^{m-}$, where X = Si^{IV}, Ge^{IV}, or P^{V} and Z = Co^{II}, Co^{III}, Ni^{II}, etc.[10].

The state of the HPA in solution is determined by the set of little investigated dissociation, disproportionation, etc. equilibria and depends on the acidity of the medium, the composition and concentration of the HPA, and the nature of the solvent. The region corresponding to their existence has been determined for a comparatively small number of HPA. The equilibration times in HPA solutions vary from a fraction of a second to several months[38].

The stability of the heteropolyanions as regards hydrolysis in aqueous solutions decreases in the sequence $W^{VI} > Mo^{VI} > V^{V}$.[10] The stability of the HPAn-Mo^{VI} decreases in the following sequence as a function of X: $Si^{IV} > Ti^{IV}$, $Zr^{IV} > Ge^{IV} > P^{V} > As^{V}$.[10] 12-Molybdophosphates exist in an acid aqueous solution at pH ≤ 1.5;[16] with increase of pH, they undergo alkaline hydrolysis, which proceeds via the following mechanism in dilute solutions ($\leq 10^{-3}$ M):[10,16]

$$PMo_{12}O_{40}^{3-} \overset{OH^-}{\rightleftarrows} PMo_{11}O_{39}^{7-} + MoO_4^{2-} \overset{OH^-}{\rightleftarrows} HP_2Mo_5O_{23}^{5-} + MoO_4^{2-} \overset{OH^-}{\rightleftarrows} HPO_4^{2-} + MoO_4^{2-}.$$

In concentrated solutions ($\sim 10^{-1}$ M) the hydrolysis proceeds via the formation of a dimeric 9-molybdophosphate $P_2Mo_{18}O_{62}^{6-}$ as an intermediate[10,16]. The polyanions with P : Mo ratios of 1 : 9, 2 : 18, and 2 : 5 predominate in the H^+–MoO_4^{2-}–HPO_4^{2-} system at pH 1.5–6.0; their stability constants have been determined[39]. In highly acidic media (pH < 1.5) the heteropolyanions undergo acid hydrolysis with formation of defective polyanions and oxomolybdenum(VI) cations[10].

The stability of HPA increases in organic media[10,12]. It has been established by the conductimetric method that acids such as PMo_{12}, PW_{12}, $SiMo_{12}$, SiW_{12}, $PMo_{11}V$, and $PW_{11}V$ are resistant to solvolysis in ethanol, acetone, and acetic acid up to concentrations in the range 10^{-6}–10^{-5} M.[40,41]. The introduction of vanadium(V) into molybdenum HPA increases their resistance to hydrolysis[42,43]. The stability of $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-n) in aqueous solutions decreases with increasing n in the sequence HPA-1 > HPA-2 > HPA-3.[42] Although HPA-n with $n > 3$ have not been isolated as individual compounds[23,44], their salts are known[38,45,46]. The most stable HPA-1 begins to hydrolyse only in 0.8 M HCl.[38] The acids HPA-n with $n > 1$ are converted into HPA-n with a smaller value of n on increase of $[H^+]$;[43] for example, the following reaction takes place for $n = 3$:

$$10H_6PMo_9V_3O_{40} + 12H^+ \rightleftarrows 9H_5PMo_{10}V_2O_{40} + 12VO_2^+ + H_3PO_4 \quad (3)$$

The first stage of the reaction of HPA-n is probably degradative dissociation:

$$H_{3+n}PMo_{12-n}V_nO_{40} + H_3O^+ \rightleftarrows VO_2^+ + H_{6+n}PMo_{12-n-1}V_{n-1}O_{39} \quad (4)$$

At pH 1–3 the acids HPA-n disproportionate[43,47]

$$2PMo_{11}V \rightleftarrows PMo_{12} + PMo_{10}V_2 \cdot \quad (5)$$

The equilibrium constant of reaction (5) is 5.5×10^{-2} at pH 2.[43] The disproportionation reaction of $PW_{11}V$ is of second order with respect to $PW_{11}V$; the rate of reaction increases with pH and ionic strength I (the rate constants are 0.69 and 22.4 litre mol^{-1} s^{-1} at 25 °C, $I = 3$, and pH 3.9 and 4.9 respectively).[48] The heteropolyblues also disproportionate[49,50] in accordance with the mechanism

$$2PW_{11}^{VI}W^{V} \rightleftarrows PW_{12}^{VI} + PW_{10}^{VI}W_2^{V}.$$

Such reactions take place very readily and probably involve electron transfer.

The 12-series polyanions PMo_6V_6 and PMo_2V_{10} are stable in moderately acid solutions (pH 2.5–5.5).[38] Using the isotopes ^{99}Mo, ^{185}W,[51,52] and ^{17}O,[34] it was shown that the ligands in the HPA exchange with the solution. The ^{99}Mo exchange between PMo_{12} (0.01 M) and $Na_2^{99}MoO_4$ (0.1 M) in aqueous solution at 20 °C and pH 1.2 takes place to the extent of 100% in 15 min.[51] The central atom does not exchange. According to ^{17}O NMR data, the oxygen atom in the M=O, M–O–M, and X–O–M bond in HPA have markedly different chemical shifts, rates of exchange with the solvent, and degrees of protonation[32-34]. The rate of ^{17}O exchange in the HPA-n ($n = 0, 1, 2$) decreases by an order of magnitude following the introduction of each successive V^{V} atom into the HPA molecule. It has been suggested that the oxygen exchange proceeds via a dissociation reaction of type (4) and via ligand exchange with the solvent.

The kinetics and mechanism of the ligand substitution in heteropolyanions have been studied[53-56]. The reaction

$$VO^{2+} + SiW_{12} \rightarrow SiW_{11}V + W^{VI}$$

in aqueous solution proceeds in accordance with the kinetic equation $w = k[SiW_{12}][OH^-]$, where $k = 2.8 \times 10^6$ litre mol^{-1} s^{-1} at 25 °C. The process proceeds via a dissociative mechanism with the rate-limiting stage

$$SiW_{12}O_{40}^{4-} + OH^- \rightarrow SiW_{11}O_{39}^{8-} + W^{VI}.$$

Next vanadium(IV) is rapidly inserted in the vacancy formed[53,54]. $SiW_{11}O_{39}^{8-}$ reacts analogously with Co^{2+}, forming $SiW_{11}O_{39}Co^{6-}$.[55] In the reaction of VO^{2+} with $PW_{12}O_{40}^{3-}$ the dissociative pathway competes with the associative pathway, which includes the formation of the complex $[(HPA).VO^{2+}]$.[54]

The rate of reaction of HPA-n (n = 0–6) with VO^{2+}, i.e.

$$PMo_{12-n}V_n^V + VO^{2+} \rightleftarrows PMo_{12-n}V_{n-1}^V V^{IV} + V^V \text{ (or } Mo^{VI}), \quad (6)$$

at pH 2.2–3.0 is described by the kinetic equation $w = k[\text{HPA-}n][VO^{2+}]/[H^+]^a$, where $1 < a < 2$.[56] The formation of the intermediate complex $[(\text{HPA-}n).VO^{2+}]$ has been noted. The reactivity of HPA-n in reaction (6) varies in the sequence HPA-0 > HPA-1 > HPA-2 > HPA-3 > HPA-4 > HPA-5 > HPA-6. The mechanism of reaction (6) depends on the composition of HPA-n. The process involving HPA-0 probably proceeds via the migration of V^{IV} to the existing vacancy in the coordination sphere of the polyanion. The reaction of HPA-1 apparently involves substitution of Mo^{VI} by V^{IV}, while the inner-sphere electron transfer from V^{IV} to HPA-n is more probable in the case of HPA-n ($n > 1$).[56] The equilibrium constants of the reaction of HPA-n with VO^{2+},

$$PMo_{12-n}V_{n-i}^V V_i^{IV} + VO^{2+} + H_2O \rightleftarrows PMo_{12-n}V_{n-i-1}^V V_{i+1}^{IV} + VO_2^+ + 2H^+ \quad (7)$$

(where $0 \leq i \leq n$, $n = 3.6$) at pH 2.0–2.7 are almost independent of n and are approximately 10^{-6} mol^2 litre^{-2},[57] i.e. HPA-n are most resistant to hydrolysis than the corresponding blues.

The kinetics and mechanism of the formation and decomposition of heteropolyanions have been investigated[58–61]. The formation of the PMo_{12} and $PMO_{10}V_2$ anions from phosphate, Mo^{VI}, and V^V in an acid aqueous solution is very rapid[59,60]. The kinetics of these reactions are complex and their mechanism is insufficiently clear.

3. Oxidation-Reduction Properties of HPA

Many HPA are fairly strong oxidants. They are reduced by various reductants both electrochemically[10] and photochemically[62,63]. Pope[64] found an empirical rule for isopolyanions and heteropolyanions of different structures, according to which the anion is reduced without decomposition when it contains M atoms linked to one terminal O atom. Such anions include those having the Keggin ($XM_{12}^{VI}O_{40}^{x-8}$) and Dawson ($X_2M_{18}^{VI}O_{62}^{2x-16}$) structures in which each M atom has one oxo-group M=O (Pope's structural type I). The heteropolyanions decompose on reduction if each M atom has a *cis*-dioxo-group O=M=O (structural type II; $XMo_6O_{24}^{x-12}$, $Mo_7O_{24}^{6-}$, etc.). Anions containing both types of M atoms (type III; $H_2W_{12}O_{42}^{10-}$) are reduced in the same way as the heteropolyanions of structural type I. This rule makes it possible to predict the structure of the polyanion on the basis of its reducing properties.

On reduction, the HPA are converted into heteropolyblues—"mixed valence" complexes which are coloured an intense blue as a result of intervalence electronic transitions. The optical density of the blues is frequently proportional to the degree of their reduction[10,50,57,65]. Correlations have been established between the changes in the energies of the spectral bands of the blues and the half-wave potentials of the reduction of the heteropolyanions and also the charge of the heteropolyanion[28,66]. Many blues have been isolated in the form of the acids or salts.

The molecular structure of the blues has not been established rigorously. Nevertheless it is generally accepted that, for a low degree of reduction, it is the same as the structure of the initial heteropolyanions[8,9,64]. This is indicated by the identity of the X : M ratios in the blues and in the initial heteropolyanions[10,67,68], the similarity of the ultraviolet absorption spectra of the blues and the heteropolyanions[67,69], electron diffraction data[69], and also the reversibility of the polarographic reduction of many Mo^{VI}, W^{VI}, and V^V heteropolyanions[10,48–50,65,70]. The exceptional ease of the heteropolyanion reduction and oxidation reactions is apparently also a consequence of the constancy of the structure of the polyanion in oxidation-reduction reactions.

Heteropolyanions are many-electron oxidants. The limiting number of electrons accepted by the HPA molecule without decomposition depends on its composiiton and the reduction conditions: it can reach six and more electrons[49,50,65,70–72]. The addition of electrons increases the basicity of the polyanion and may be accompanied by its protonation[49,50,65,70]. The oxidative properties of HPA are closely related to their acid properties. The degree of protonation of the heteropolyanion increases with increasing basicity of the initial heteropolyanion and the degree of reduction and with decrease of the pH of the medium. These data have been obtained in the study of the dependence of the half-wave potential of the polarographic reduction of the heteropolyanions on the pH.[49,50,65,70]. The reduction of the Mo^{VI} or W^{VI} heteropolyanions can be represented by the equation

$$XM_{12}^{VI}O_{40}^{x-8} + p\,e^- + q\,H^+ \rightarrow H_qXM_{12-p}^{VI}M_p^VO_{40}^{x+q-p-8}, \quad (8)$$

where $q \leq p$. On reduction in an acid aqueous solution (pH ≤ 1), the HPAn-W^{VI} of the 12-series can have a charge up to −6 without the addition of a proton, while in a neutral medium the charge can be up to −9. The corresponding values for the more stable $X_2W_{18}O_{62}^{2x-16}$ heteropolyanions are −8 and −12.[49] The heteropolyanions are protonated preferentially on reduction at the bridging O atoms probably in the angular M–O–M linkages[73,74]. As a rule, the molybdenum and tungsten blues are more resistant to hydrolysis than the initial heteropolyanions[49].

Many studies have been devoted to the location of the added electrons in the blues[50,65,66,73–80]. According to the results obtained by spectroscopic and magnetic methods, the electrons are located in the blues at the metal ions (without the formation of a many-centre molecular orbital). There is then thermal oscillation of the electrons between all the equivalent states at frequencies $\geq 10^8$ s^{-1}; the oscillation decays at a temperature close to that of liquid helium[75,76,80]. Such oscillation probably occurs via tunnel electron transitions between the metal ions in different oxidation states.

The oxidative properties of HPA depend on the nature of both the ligands and the central atom. The standard oxidation potentials of HPA are unknown because the equilibria in their solutions have not been investigated. Instead one uses the formal potentials ϕ^0 which depend on the pH and [HPA].[11,81] The potentials ϕ^0 are considered below relative to the normal hydrogen electrode.

The oxidation potential of the HPA is lower than the potential of the ligands in the polyanion; the HPA and ligand potentials then vary in parallel. The oxidising capacity decreases in the sequences[69,82,83]

$$\text{HPA-}V^V > \text{HPA-}Mo^{VI} > \text{HPA-}W^{VI};$$
$$VO_3^- > MoO_4^{2-} > WO_4^{2-}.$$

The central constant-valence ion influences the HPA potential via a change in the charge of the polyanion[83]. The oxidation potential of the heteropolyanion decreases with increasing ionic charge in the sequence

$$PW_{12}O_{40}^{3-}(0.15) > SiW_{12}O_{40}^{4-}(-0.05) \simeq GeW_{12}O_{40}^{4-}(-0.02) > BW_{12}O_{40}^{5-}(-0.36);$$

the reduction potentials (V) of the heteropolyanions at a graphite cathode in 1 M H_2SO_4 are given in brackets[76]. The oxidation potential of the HPA increases if X is a strong oxidant. Thus the reduction of $Co^{III}W_{12}O_{40}^{5-}$ to $Co^{II}W_{12}O_{40}^{6-}$ is characterised by $\phi^0 \cong 1$ V.[48,84]. The electrochemical reduction of $Fe^{III}W_{12}O_{40}^{5-}$ gives rise to a blue with Fe^{III} and not Fe^{II}.[50]

The oxidative properties of HPA-*n*, widely used as catalysts of liquid-phase oxidation, are of great interest. The introduction of vanadium(V) into HPA-Mo increases the oxidation potential of the HPA.[82,83,85]. It has been established by EPR that, on reduction of HPA-*n*, the electrons are located at the vanadium atoms[78]. The blues HPA-*n* dissociate in solution with elimination of VO^{2+}; the degree of degradative dissociation falls with decrease of *n* and with increase of pH.[86]

Fig. 2 illustrates the dependence of the HPA-*n* potential on the degree of reduction[81,87]. The reduction of HPA-*n* with $n = 1-4$ at pH 1 is characterised by a single jump of the potential $\phi^0 = 0.68-0.71$ V, which corresponds to the conversion of the entire vanadium(V) into vanadium(IV) in the heteropolyanion. The reduction process consists of a sequence of one-electron stages occurring at a single potential. The absence of individual one-electron stages can be explained by the protonation of the heteropolyanion in accordance with Eqn.(8), as a consequence of which the charge of the polyanion remains unaltered on its reduction[11]. The reduction of $PW_{12-n}V_nO_{40}^{(3+n)-}$ takes place analogously[48]. The oxidising capacity of HPA-*n* is somewhat inferior to that of the VO_2^+ ion, for which $\phi^0 = 0.87$ V at pH 1.[88] However, in contrast to the one-electron oxidant VO_2^+, the HPA-*n* is a complementary partner for one-, two-, and many-electron reductants. This makes it possible to employ the HPA-*n* as catalysts of a wide variety of oxidation reactions.

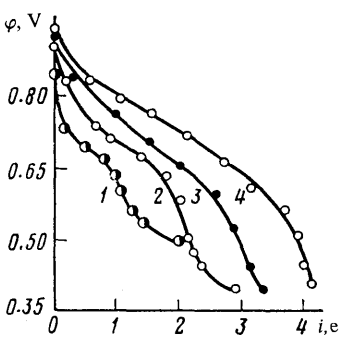


Figure 2. Dependence of the oxidation potential of HPA-*n* on the degree of reduction *i* (relative to the normal hydrogen electrode, pH 1.1, reductant—hydrazine):[81,87] *1*) $n = 1$; *2*) $n = 2$; *3*) $n = 3$; *4*) $n = 4$.

4. HPA as Oxidants Acting Reversibly

The application of HPA in homogeneous oxidative catalysis is based in many instances on their capacity for being reversibly oxidised [Eqns.(1) and (2)].[1,2] The thermodynamic condition for the occurrence of reactions (1) and (2) is

$$\varphi^0_{Red} < \varphi^0_{HPA} < \varphi^0_{O_2} = 1.23\text{V}.$$

The "mixed-ligand" HPA of structural type (I), such as HPA–Mo–V, HPA–W–V,[1,2] and HPA–Mo–W,[89] are reversibly oxidisable in the range of potentials ϕ^0 of interest for homogeneous catalysis. The HPA-*n* ($PMo_{12-n}V_n$, $n = 2-6$) have been studied in greatest detail. HPA-*n* containing at least two V atoms are reversible-action oxidants. The Mo and V heteropolyacids incorporating ligands of the same type do not have this property because their blues are hardly oxidised by the oxygen in solution. The W blues are readily oxidised by oxygen in solution[90] and are oxidised even by water (with liberation of H_2).[91] However, the HPA-W have a potential which is too low for their employment in oxidative catalysis. It is noteworthy that crystalline monometallic HPA, for example PMo_{12}, becomes reversible oxidants under more severe conditions at 200–300 °C (see Section IV).

The central atom does not exert a significant influence on the reversible oxidisability of the HPA. Furthermore, its presence is sometimes not required for the occurrence of reactions (1) and (2). For example, the mixed Mo–V isopolycompounds are reversible-action oxidants[92]. Among all the HPA having this property, the HPA-*n* are of greatest interest because of the ease of their preparation, their stability in solution, and their high reactivity.

We shall now consider the mechanism of reactions (1) and (2). It has been suggested that the true oxidants in reaction (1) are one-electron oxidants, namely the VO_2^+ ions formed as a result of the reversible dissociation reaction (4).[93] However, this mechanism is not general. The electrochemical reduction of the HPA can proceed either via successive one-electron transfers or via the simultaneous transfer of several electrons[48,49,65,70]. The oxidation of the test reagent Ph(t-Bu)CHOH by HPA-6 in aqueous solution proceeds preferentially (to the extent of 67%) via a heterolytic mechanism involving oxidation by polyanions and partly (to the extent of 33%) via a homolytic mechanism involving oxidation by VO_2^+ ions[94].

The free VO^{2+} ion is oxidised by oxygen only at pH $\geq$ 2.5. The degrees of conversion of $VOSO_4$ (0.01 M) at 14 °C after 1 week at pH 2.5 and 3.5 are 1.5 and 21% respectively[95]. In more acid media vanadium(IV) can be oxidised via reaction (2) only when it is part of the composition of the heteropolyanion. It follows from the potentials for the HPA-*n* ($\phi^0 \geq 0.68$ V) and ϕ^0 ($O_2/HO_2^\cdot$) = −0.32 V [96] that the one-electron oxidation of the blues H_i(HPA-*n*) with formation of the free radical $HO_2^\cdot$ is thermodynamically unfavourable[97–100]. The mechanism of reaction (2) depends on *i*—the degree of reduction of the blue. The blues H_i(HPA-*n*) with i, $n \geq 4$ are oxidised via the transfer of four electrons in the complex of H_i(HPA-*n*) with O_2 without the release of the free radicals into space[97–99]. For $i < 4$, free radicals are formed in reaction (2), which is indicated by the detection of acetone when reaction (2) is carried out in the presence of isopropyl alcohol[97].

The mechanism of reaction (2) was specified in detail in the study of the kinetics of the oxidation of weakly reduced blues with $i < 1$.[100] Such values of *i* are in fact usually observed in catalytic processes involving HPA-*n*. The solution of the blue then contains the anions H_1(HPAn-*n*) and HPAn-*n*. The mechanism of reaction (2) is examined below in relation to the oxidation of H_i(HPA-3).

For $i < 1$, the oxidation of H_i(HPA-3) proceeds in accordance with the kinetic equation

$$w = k[V^{IV}]^3[O_2]/[HPAn\text{-}3]^2 \qquad (9)$$

which corresponds to the mechanism

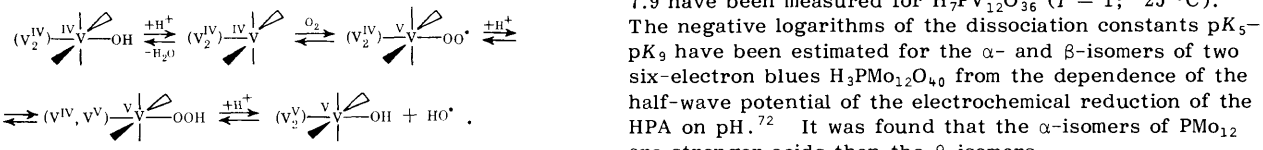
$$2PMo_9V_2^VV^{IV} \rightleftarrows PMo_9V_3^V + PMo_9V^VV_2^{IV}; \qquad (10)$$

$$PMo_9V^VV_2^{IV} + PMo_9V_2^VV^{IV} \rightleftarrows PMo_9V_3^V + PMo_9V_3^{IV}; \qquad (11)$$

$$PMo_9V_3^{IV} + O_2 + 3H^+ \xrightarrow{\text{slow}} PMo_9V_3^V + H_2O + HO^\cdot \quad (12)$$

$$PMo_9V_2^VV^{IV} + HO^\cdot + H^+ \rightarrow PMo_9V_3^V + H_2O,$$

where $PMo_9V_3^V$ = HPAn-3. Stages (10) and (11) are rapid disproportionation reactions which apparently proceed via electron transfer. The rate-limiting stage (12) includes the formation of a vacancy in the coordination sphere of H_3(HPA-n). Next a complex of H_3(HPA-n) with O_2, in which successive transfer of three electrons accompanied by the addition of H^+ takes place, is formed:



The complex of the heteropolyanion with O_2 apparently has a linear or angular structure.

The rate of oxidation of H_i(HPA-n) with $n > 3$ decreases in the sequence H_i(HPA-3) > H_i(HPA-4) > H_i(HPA-6), which can be explained by the increase of ϕ^0 for HPA-n in the same sequence (Fig.2).[100] The oxidation of H_i(HPA-2) proceeds similarly to the reaction with H_i(HPA-3) and is described by the kinetic equation (9). The process probably involves the disproportionation reaction

$$2PMO_{10}V_2 \rightleftarrows PMo_9V_3 + PMo_{11}V,$$

which is indicated by the fact that the three-electron mechanism is more favourable than the two-electron mechanism[10]. The latter has also been confirmed by the thermodynamic data for the reduction of HPA-n (Fig.2) and O_2.[101] The two-electron mechanism apparently operates in the oxidation of $SiW_{10}^{VI}W_2^V$ by water with evolution of hydrogen[91].

5. The Acid Properties of HPA

Heteropolyacids are strong Brønsted acids[8-10,15]. Their strength is much greater than that of simple acids formed by the corresponding heteroatoms[102]. The basicity of the HPA, which follows from the Keggin structure $H_{8-x}X^xM_{12}^{VI}O_{40}$, has been demonstrated by numerous direct measurements[10,23,85,102-104]. When Mo^{VI} or W^{VI} is substituted by V^V and on reduction of the HPA, the basicity increases by unity for each V^V ion and for each electron added. An increase of basicity is accompanied by a decrease of the acid strength of the HPA.[8-10,102,103].

Information about the proton structure of the HPA hydrates has been obtained mainly by broad-line ^1H NMR.[73,74,105-107]. Two types of protons have been found in the HPA molecules: the non-localised hydrated and localised unhydrated H^+. The former are linked to the polyanion as a whole and rapidly exchange with the protons of the water molecules in the hydration shell of the HPA. The protons of the second type appear on reduction of the HPA and on substitution of Mo^{VI} or W^{VI} by V^V. These protons are more strongly bound to the HPA and are located at the O atoms of the angular M–O–M bonds. Analogous conclusions have been reached on the basis of ^{17}O NMR data for HPA solutions[33,34].

The available acid dissociation constants of the HPA are limited as a consequence of the instability of many polyanions in solution. In aqueous solution the stepwise nature of the first three dissociations of the HPA is usually undetectable as a consequence of the levelling influence of the solvent[15,108,109]. Non-aqueous solvents have a differentiating effect on the dissociation of the HPA.[103]

According to conductimetric data, the acids $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$ in aqueous solution are strong 1–4 and 1–5 electrolytes respectively[104]. The average $pK_{1-4} = 0.75$ was found for $H_4PMo_{11}VO_{40}$.[42] In $H_5PMo_{10}V_2O_{40}$, $H_6PMo_9V_3O_{40}$, and $H_7PV_{12}O_{36}$ the first three protons are split off completely, while the remaining are split off in steps (as the pH is increased). $pK_4 = 1.16$ and $pK_5 = 2.14$ have been found for $H_5PMo_{10}V_2O_{40}$ and $pK_4 = 1.25$, $pK_5 = 1.62$, and $pK_6 = 2.00$ have been found for $H_6PMo_9V_3O_{40}$ ($I = 0$; 25 °C).[109] $pK_4 = 3.4$, $pK_5 = 4.9$, $pK_6 = 6.4$, and $pK_7 \cong 7.9$ have been measured for $H_7PV_{12}O_{36}$ ($I = 1$; 25 °C).[108] The negative logarithms of the dissociation constants pK_5–pK_9 have been estimated for the α- and β-isomers of two six-electron blues $H_3PMo_{12}O_{40}$ from the dependence of the half-wave potential of the electrochemical reduction of the HPA on pH.[72] It was found that the α-isomers of PMo_{12} are stronger acids than the β-isomers.

Table 1. The acid dissociation constants of HPA in non-aqueous media at 25 °C and $I = 0$ (the pK_i were estimated from the Bjerrum equation).[40,41]

Acid	Acetone			Ethanol			Acetic acid	Acid	Acetic acid
	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3	pK_1		pK_1
H_3PW_{12}	(1.6)	(3.0)	3.98	(1.6)	(3.0)	4.10	4.77; 4.75 [103]	H_4GeW_{12}	4.25 [103]
$H_4PW_{11}V$	(1.8)	(3.2)	4.37	—	—	—	4.74	$H_5GeW_{11}V$	4.65 [103]
$H_5PW_{10}V_2$	—	—	—	—	—	—	4.78	$H_6GeW_{10}V_2$	4.60 [103]
H_4SiW_{12}	(2.0)	3.61	(5.3)	(2.0)	3.96	(6.3)	4.97; 4.75 [103]	$HClO_4$	4.87 [113]
								HBr	5.6 [113]
H_3PMo_{12}	(2.0)	3.62	(5.3)	(1.8)	3.41	(5.1)	4.70	H_2SO_4	7.0 [113]
$H_4PMo_{11}^{VI}Mo^V$	(2.1)	3.69	(5.5)	(1.9)	3.77	(5.9)	—	HCl	8.4 [113]
$H_4PMo_{11}V$	(2.1)	3.73	(5.6)	(1.9)	3.74	(5.8)	4.68	HNO_3	10.1 [113]
H_4SiMo_{12}	(2.1)	3.90	(5.9)	—	—	—	4.78		

Note. The dissociation constant of PW_{12} in ethanol were measured conductrimetrically as in the study of Kulikov and Kozhevnikov[41]. $pK_1 = 4.0$ for HCl in acetone[88] and $pK_1 = 3.57$ for HNO_3 in ethanol[88].
The numbers in square brackets here and in Table 2 denote references (Ed.of Translation).

The acidity of the HPA has been studied more widely in non-aqueous media[40,41,103,110]. In such media the heteropolyanions are much more resistant to solvolysis[10,12]. Table 1 lists the thermodynamic dissociation constants of the HPA in ethanol, acetone, and acetic acid, measured conductrimetrically[40,41] and potentiometrically[103]. In acetone and ethanol, which are solvents of moderate polarity, the first proton of all the HPA and also the second proton in $H_3PW_{12}O_{40}$ and $H_4PW_{11}VO_{40}$ are fully dissociated at concentrations in the range 10^{-6}–10^{-3} M. The subsequent protons are only partly dissociated. In the weakly polar acetic acid the HPA behave as monobasic acids whose strength is similar to that of $HClO_4$.[40,41]

The weak dependence of the acid strength of the HPA on their composition is striking. This is due to the large size of the heteropolyanion and the unusual proton structure of the HPA.[40,41,105,109]. In aqueous and non-aqueous solutions the HPA consist of solvate-separated ion pairs $H^+(H_2O)_m \| HPAn^-$, in which the protons are hydrated and linked to the anion as a whole and not to a specific centre in the heteropolyanion[40,41]. The structure of the HPA is satisfactorily consistent with the model consisting of a

charged sphere with a large radius on the surface of which the acid protons are accommodated (with a minimal electrostatic repulsion energy) in the form of point charges[40,41].

The acidity of HPA-W is greater than that of HPA-Mo,[41,107,111] which agrees with the higher negative charge on the O atoms in HPA-Mo compared with HPA-W.[111] According to X-ray electronic spectroscopic data, the effective charges in the PMo_{12} heteropolyanion are distributed as follows: $[P^{2.5+}Mo_{12}^{1.1+}O_{40}^{0.43-}]^{3-}$.[111] The HPA are much stronger than the usual inorganic acids, which is true of both dilute and concentrated HPA solutions. The acidity of concentrated aqueous and non-aqueous $H_3PW_{12}O_{40}$ solutions (≤50 wt.%) is higher than that of $HClO_4$ and H_2SO_4 solutions by 1–1.5 units of the Hammett acidity function H_0.[112]

III. HETEROPOLYACIDS AS LIQUID-PHASE OXIDATION CATALYSTS

The liquid-phase oxidation reaction takes place in solutions in the presence of HPA-*n* or their soluble salts and more rarely other mixed HPA capable of being reversibly oxidised. The stages of the catalytic process—reactions (1) and (2)—can be carried out simultaneously in a single reactor or separately. In the latter case contact between the organic substrates and O_2 is eliminated. The catalysts may be the HPA-*n* themselves (one-component systems) or in combination with other compounds (two-component systems). Among the latter, the HPA-*n* + Pd^{II} system is of greatest importance. Homogeneous catalysts based on HPA consist as a rule of complex equilibrium mixtures of polyanions of different compositions with products of the degradative dissociation of the heteropolyanion. A common deficiency of homogeneous catalysts is the difficulty of separating the reaction products from the catalyst when high-boiling products are formed. The reactions in which the HPA-*n* are used as one- and two-component catalysts are considered below and the mechanism of their catalytic action is discussed.

1. One-Component Systems

(*a*) *Oxidation of sulphur compounds.* The oxidation of H_2S, SO_2, and mercaptans catalysed by HPA-*n* is promising for the elimination of sulphur compounds from industrial and natural gases, while the oxidation of alkyl and aryl sulphides is promising for the industrial synthesis of sulphoxides and sulphones[114–118]:

$$H_2S + 1/2O_2 \xrightarrow[H_2O,20^\circ C]{\text{HPA-}n} S + H_2O\ ; \qquad (13)$$

$$SO_2 + 1/2O_2 + H_2O \xrightarrow[H_2O,20^\circ C]{\text{HPA-}n} H_2SO_4\ ; \qquad (14)$$

$$2RSH + 1/2O_2 \xrightarrow[80^\circ C]{\text{HPA-}n} RSSR + H_2O\ ; \qquad (15)$$

$$R_2S + 1/2O_2 \xrightarrow[Me_2CO,120^\circ C]{\text{HPA-}n} R_2SO\ ; \qquad (16)$$

$$R_2SO + 1/2O_2 \xrightarrow[Me_2CO,120^\circ C]{\text{HPA-}n} R_2SO_2\ . \qquad (17)$$

In reaction (13) HPA-6 has a selectivity of ~97%; ~3% of H_2S is oxidised to H_2SO_4.[116] Reactions (16) and (17) are highly selective—up to 100% with respect to the sum of R_2SO and R_2SO_2 for a 100% degree of conversion of the sulphide[115]; on this basis, a non-radical mechanism has been proposed for these processes[115]. However, subsequent studies established that the oxidation of diethyl sulphide with $^{18}O_2$ leads to the formation of a sulphoxide enriched in the ^{18}O isotope to the extent of 44–54%. It has also been shown that, in the absence of oxygen, HPA-*n* does not oxidise Et_2S and Et_2SO to the sulphone. These data indicate a radical mechanism of reactions (16) and (17).[119]

(*b*) *Bromination of aromatic compounds.* It has been recently established[120] that HPA-*n* catalyse the oxidative bromination of arenes in the ring with participation of HBr as the brominating agent and O_2 as the oxidant. In the case of arenes, namely benzene, its derivatives, naphthalene, thiophen, etc., the process takes place in the HOAc–H_2O–H_2SO_4 solution at 50–100 °C and includes the following stages:

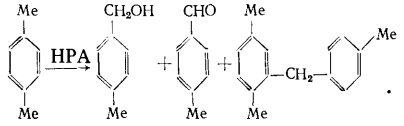
$$2HBr + HPA\text{-}n + 2H^+ \rightarrow Br_2 + H_2(HPA\text{-}n); \qquad (18)$$

$$\begin{gathered} ArH + Br_2 \rightarrow ArBr + HBr \\ H_2(HPA\text{-}n) + 1/2O_2 \rightarrow H_2O + HPA\text{-}n. \end{gathered} \qquad (19)$$

Reaction (18) takes place readily in the absence of ArH. The presence of stage (19) has been confirmed by the similarity of the isomeric compositions of the products and of the relative rates of oxidative bromination and the bromination of ArH by molecular bromine. The oxidative bromination has the advantage that one can use Br^- ions instead of Br_2 in the reaction, but it suffers from the disadvantage that the alkyl substituents in ArH are oxidised in a side reaction.

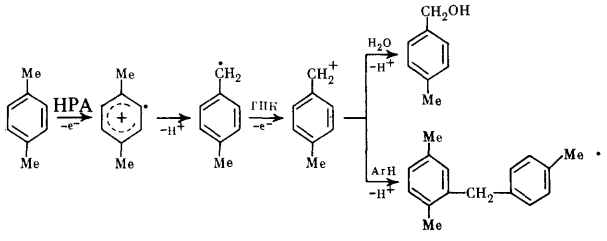
The halogenation of arenes by HCl and HI does not take place under analogous conditions, because the oxidation potential of HPA-*n* is insufficiently high for the oxidation of HCl to Cl_2; the I^- ion is readily oxidised by HPA-*n* to I_2 but I_2 is too weak as an iodinating agent.

(*c*) *Oxidation of hydrocarbons.* Heteropolyacids with a sufficiently high oxidation potential oxidise alkyl substituents in the aromatic ring[121–123]. Thus $K_5Co^{III}W_{12}O_{40}$ oxidises methylbenzenes under heterogeneous conditions in a non-catalytic process to a mixture of aldehydes, alcohols, and diarylmethanes[121]:



This reaction has been carried out catalytically using HPA-*n*.[120] In acetic acid in the presence of $K_5CoW_{12}O_{40}$ and potassium acetate, methylbenzenes undergo ring acetoxylation[123].

The proposed mechanism involves electron transfer from ArH to HPA with formation of an aromatic radical-cation whose reactions give rise to benzyl alcohol and diarylmethane[120,121]:



The alcohol undergoes further oxidation with formation of the aldehyde. When H is replaced by D in the methyl group, a large isotope effect is observed ($k_H/k_D = 6$), showing that the proton is removed from the radical-cation in the rate-limiting stage.

Heteropolyacids of different compositions have been used as catalysts of the liquid-phase oxidation of tetralin[124] and olefins[125].

(*d*) *Epoxidation of olefins by aromatic hydroperoxides.* The salts of HPA-Mo are effective catalysts of the industrially important reaction in which olefins are epoxidised by organic hydroperoxides[126–128]:

$$RCH=CH_2 + R'OOH \xrightarrow[80\sim110^\circ C]{HPA} RCH-CH_2 + R'OH \quad (20)$$

The application of the HPA themselves is undesirable because they catalyse the acid decomposition of organic hydroperoxides[129]. The mechanism of the epoxidation of olefins has been examined[128,130,131]. Molybdenum compounds are in many instances the most active catalysts. The true catalysts are probably the glycol complexes of molybdenum(VI) formed in the reaction mixture regardless of the initial ligand environment and the degree of oxidation of the metal[130,132].

The epoxidation of hex-1-ene by cumenyl hydroperoxide in isopropyl alcohol in the presence of $Na_3PMo_{12}O_{40}$ takes place without an inductive period and with a selectivity close to 100%.[133] A mechanism including rapid degradative dissociation of $PMo_{12}O_{40}^{3-}$ with formation of monomeric molybdenum(VI) and a defective heteropolyanion has been proposed on the basis of kinetic data and the study of the composition of the spent catalyst:

$$PMo_{12}O_{40}^{3-} \rightleftarrows HPAn' + nMo^{VI}.$$

The molybdenum(VI) monomers are active in reaction (20), although one cannot fully rule out also catalysis by HPAn' species. The catalytic activity of HPAn-Mo decreases slightly in the sequence $PMo_{12} > SiMo_{12} \cong PMo_{11}V$, in which the resistance of the heteropolyanion to hydrolysis increases; HPAn-Mo is much more reactive than HPAn-W.[133]

2. Two-Component Catalysts

(a) The HPA-n + Pd^{II} system. The HPAn-*n* + Pd^{II} system belongs to the class of the most important catalysts of liquid-phase oxidation based on HPA-*n*. It is highly selective in many reactions involving the oxidation of organic substances by palladium(II) salts:

$$S + Pd^{II} \rightarrow P + Pd^0, \quad (21)$$

where S and P are the substrate and reaction products. All the catalytic processes presented in Table 2 are based on a combination of reactions (21), (1), and (2) in which Red = Pd^0 and Ox = Pd^{II}. Among these, the oxidation and acetoxylation of olefins, the oxidation of alcohols, the oxidative coupling of organic compounds etc. are reactions of practical importance[1,2]. The applications and the mechanism of the action of the HPA-*n* + Pd^{II} system have been examined in a number of reviews[1,2,6,134,135].

Analogous catalytic systems based on other oxidants acting reversibly, such as Cu^{II}, Fe^{III}, NO_3^-, etc. are known[136–138]. Among them, $CuCl_2$ is of greatest importance:

$$Pd^0 + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl;$$
$$2CuCl + 1/2O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O.$$

A deficiency of the $CuCl_2$ + Pd^{II} redox system is its secondary chlorinating activity, the pronounced corrosion of the apparatus, and also the low catalytic activity of palladium(II). Like stronger oxidants, the HPA-*n* are capable of oxidising palladium(0) to palladium(II) in the absence of Cl^- ions. The HPA-*n* + Pd^{II} system is therefore free from the above deficiencies[1,2,6].

It has been established that many reactions catalysed by the HPA-*n* + Pd^{II} system proceed mainly via a multistage heterolytic mechanism with stages (21), (1), and (2).[2] Thus the oxidation of isopropyl alcohol in aqueous solution proceeds preferentially via the following stages[139,140]:

$$Me_2CHOH + Pd^{II} \rightarrow Me_2CO + Pd^0 + 2H^+;$$
$$Pd^0 + HPA\text{-}n + 2H^+ \rightarrow Pd^{II} + H_2(HPA\text{-}n);$$
$$H_2(HPA\text{-}n) + 1/2O_2 \rightarrow HPA\text{-}n + H_2O.$$

However, the radical pathway in the oxidation of the substrate, due to the intermediate formation of the HO$^\cdot$ free radicals in reaction (2), may also make an appreciable contribution under certain conditions[97,139,140], for example:

$$Me_2CHOH + HO^\cdot \rightarrow Me_2\dot{C}OH + H_2O;$$
$$Me_2\dot{C}OH + O_2 \rightarrow MeCOO^\cdot;$$
$$\mid OH$$
$$Me_2COO^\cdot + H_i(HPA\text{-}n) \rightarrow Me_2CO + H_2O_2 + H_{i-1}(HPA\text{-}n).$$
$$\mid OH$$

Table 2. The liquid-phase oxidation reactions catalysed by the HPA + Pd^{II} system [Pd^{II} in the form of $PdSO_4$, $Pd(OAc)_2$, or $PdCl_2$].

Reaction	Substrate	HPA
$RCH=CH_2 + {}^1/_2O_2 \xrightarrow[H_2O]{20\sim110^\circ C} RCCH_3$ (O)	C_2-C_8 α-olefins	HPA-*n* (*n*=2–6) [141–14]; $H_3PW_6Mo_6O_{40}$ [89]
$RCH=CH_2 + HOAc + {}^1/_2O_2 \xrightarrow[HOAc]{90\sim125^\circ C} R(AcO)C=CH_2 + H_2O$	R=H, *Me*	HPA-6 [146]
$C_2H_4 + HOAc + {}^1/_2O_2 \xrightarrow[HOAc]{20\sim40^\circ C} AcOCH_2-CH_2OH$	ethylene	HPA-6 [147]
$R_1R_2CHOH + {}^1/_2O_2 \xrightarrow[H_2O]{90\sim125^\circ C} R_1R_2C=O + H_2O$	R_1=H, R_2=Me, Pr; R_1=Me, R_2=Et; R_1, R_2=Me	HPA-*n* (*n*=2–6) [140, 148]
$ArH + HOAc + {}^1/_2O_2 \xrightarrow[HOAc]{90^\circ C} ArOAc + H_2O$	ArH = benzene, toluene	HPA-*n* (*n*=2–6) [149]
$2ArH + {}^1/_2O_2 \xrightarrow[HOAc]{50\sim90^\circ C} Ar-Ar + H_2O$	ArH = PhR (R=H, Me, Et, iso-Pr, *n*-Pr, OMe, OPh, NMe_2, Cl, COOH, CF_3), *o*-, *m*-, *p*-xylene, mesitylene, durene, thiophen, furan, sylvan	HPA-2, $H_6SiW_{10}V_2O_{40}$ [150–152]
$ArH + C_2H_4 + {}^1/_2O_2 \xrightarrow[DMF]{90^\circ C} ArCH=CH_2 + H_2O$	ArH = benzene, thiophen, furan	HPA-2, HPA-3 [153]
$R_1R_2CHCHR_3COR_4 + {}^1/_2O_2 \xrightarrow[H_2O]{60\sim70^\circ C} R_1R_2C=CR_3COR_4 + H_2O$	R_1-R_4 = H, alkyl, aryl, etc.	HPA-2 [154]

In acid solutions the oxidants for palladium(0) in reaction (1) are apparently heteropolyanions (complementary oxidation) and the VO_2^+ ions formed on dissociation of the heteropolyanion in accordance with Eqn.(4) (non-complementary oxidation).[135] The relative contributions of the heteropolyanions and VO_2^+ to reaction (1) are unknown, because the equilibrium constants of reaction (4) are not available and there are no data concerning the state of VO_2^+ in HPA-*n* solutions. The VO_2^+ ions probably form complexes with HPAn-*n*, which may influence the reactivity of VO_2^+. The question of the value of $\phi^0(Pd^{II}/Pd^0)$ has been discussed[1,6] in connection with the choice of HPA as an oxidant acting reversibly.

Apart from the HPA-*n*, other vanadium-containing HPA-Mo and HPA-W with central Si^{IV}, As^V, etc. atoms can also be used in combination with Pd^{II}.[2] It has been found recently that HPA having the composition $H_3PMo_{12-n}W_nO_{40}$ can be used as reversible-action oxidants in the oxidation of but-1-ene to ethyl methyl ketone. The catalyst incorporating $PdSO_4$ + $H_3PMo_6W_6O_{40}$ is the most active[89]. In principle there is also a possibility of employing HPA analogously in processes involving $PtCl_4^{2-}/Pt^0$ or $PtCl_6^{2-}/PtCl_4^{2-}$, but so far no examples of such reactions are known.

(b) The HPA-n + Tl^{III} system. The non-catalytic oxidation of unsaturated hydrocarbons by thallium(III) salts is used widely in preparative organic chemistry[155]. The

reactions cannot be catalysed because of the difficulty of oxidising thallium(I) to thallium(III) with oxygen. The possibility of oxidising thallium(I) to thallium(III) with oxygen in the presence of copper(II) and iron(III) halides has been noted in a number of patents[156,157].

It has been found that HPA-*n* (n = 2–8) easily oxidise thallium(I) to thallium(III) in aqueous acid or aqueous acetic acid solutions in the presence of Br^- ions[158]. The role of the Br^- ions reduces to diminishing $\phi^0(Tl^{III}/Tl^I)$ as a result of the formation of the thallium(III) bromide complex:

$$TlBr + HPA\text{-}n + 2HBr \rightarrow TlBr_3 + H_2(HPA\text{-}n). \quad (22)$$

Since H_2(HPA-*n*) is rapidly oxidised by oxygen, the HPA-*n* + $TlBr_3$ system can serve as a catalyst of the oxidation of organic substances by oxygen. An example of such a reaction is provided by the bromination of C_6–C_8 olefins with formation of dibromoalkanes and bromohydrins[158]. Further studies of the HPA-*n* + Tl^{III} redox system with other ligands, ensuring the formation of oxygen derivatives of the substrate being oxidised, are desirable.

(*c*) *The HPA-n + Ru^{IV} and HPA-n + Ir^{IV} systems.* Alkanes are oxidised by HPA-6 in aqueous solution in the presence of ruthenium(IV) and iridium(IV) chloride complexes (pH 1; 100–120 °C).[159] The oxidation of propane yielded acetone. The rate of oxidation of the t-C–H bond is higher than that of the s-C–H bond. The reaction mechanism has not been investigated, but it is probably analogous to the mechanism of the oxidation of alkanes by the Cr^{VI} + Ru^{IV} system[159].

(*d*) *The HPA-n + I_2 system.* The ability of I_2 to add rapidly and reversibly to the double bond of an olefin and the ease of the oxidation of I^- to I_2 by HPA-*n* constitute the basis of the application of the HPA-*n* + I_2 system in the oxidation of olefins to glycol ethers[160]:

$$CH_3CH{=}CH_2 + HOAc + 1/2O_2 \xrightarrow[HOAc]{HPA\text{-}6+I_2} \underset{\underset{OAc}{|}}{\overset{\overset{OH}{|}}{CH_3CH{-}CH_2}} .$$

The catalytic process can be represented by the following stages:

$$CH_3CH{=}CH_2 + I_2 + H_2O \rightleftarrows \underset{\underset{I}{|}}{\overset{\overset{OH}{|}}{CH_3CH{-}CH_2}} + HI; \quad (23)$$

$$\underset{\underset{I}{|}}{\overset{\overset{OH}{|}}{CH_3CH{-}CH_2}} + HOAc \rightarrow \underset{\underset{OAc}{|}}{\overset{\overset{OH}{|}}{CH_3CH{-}CH_2}} + HI; \quad (24)$$

$$2HI + HPA\text{-}6 \rightarrow H_2(HPA\text{-}6) + I_2; \quad (25)$$

$$H_2(HPA\text{-}6) + 1/2O_2 \rightarrow HPA\text{-}6 + H_2O. \quad (26)$$

Stage (24) is apparently rate-limiting[160]. Instead of HPA-*n*, it is possible to use also other oxidants acting reversibly. The most active catalyst is $CuCl_2$ + I_2; here copper(II) acts as an electrophile in collaborating in the elimination of the halogen from the carbon atom in stage (24).[160] The catalysis by metal complexes in halide ion elimination reactions has been examined[161].

IV. HETEROPOLYACIDS AS CATALYSTS OF HOMOGENEOUS REACTIONS OF THE ACID TYPE

The likely usefulness of the HPA as acid catalysts is determined by their high Brønsted acidity. In aqueous solutions which level off the acidities of strong acids, the HPA have no significant advantages over the usual inorganic acids. However, in non-aqueous media which differentiate acidities, the HPA proved to be much more effective than inorganic acid, because under such conditions their acidities are higher. In reactions of the acid type oxidising properties are usually harmful, since the acidity of the HPA is lowered when they are reduced. The HPA-W are therefore preferable to the HPA-Mo, because the former compounds are stronger acids and weaker oxidants than the latter.

1. Hydration and Esterification of Olefins

The hydration of olefins constitutes an industrial method of synthesising alcohols (particularly ethanol and isopropyl alcohol):

$$RCH{=}CH_2 + H_2O \overset{H^+}{\rightleftarrows} \underset{\underset{OH}{|}}{RCHCH_3} . \quad (27)$$

The reaction is carried out at an elevated pressure ensuring the displacement of equilibrium (27) to the right. The application of the HPA-W on solid carriers as heterogeneous catalysts of the hydration of olefins has been known for a long time[162,163]. Thus $H_4SiW_{12}O_{40}$ and $NaH_3SiW_{12}O_{40}$ (10^{-5}–10^{-3} M) catalyse the hydration of C_2–C_4 olefins in aqueous solution at temperatures in the range 170–350 °C and pressures in the range (1–5) × 10^4 kPa.[164] The reaction is carried out in the presence of silicic acid at a concentration of 0.5–4.5 g litre^{-1}, which increases the stability and activity of the catalyst. The process selectivity reaches 95–99% and the alcohol content in the reaction mixture is 8–12%.

The analogous reaction of C_3–C_{20} olefins in solution in carboxylic acids in the presence of 10^{-4}–10^{-2} M HPA-Mo or HPA-W at 20–140 °C leads to the formation of esters[165,166]:

$$RCH{=}CH_2 + HOAc \xrightarrow{HPA} \underset{\underset{OAc}{|}}{RCHCH_3} . \quad (28)$$

The selectivity of reaction (28) reaches 100% for a 90% conversion of the olefin.

The formation of 2-hexyl acetate from hex-1-ene solution in acetic acid proceeds in accordance with the kinetic equation:

$$w = k_1[HPA][C_6H_{12}] - k_{-1}[HPA][ester],$$

where k_1 = 0.23 litre mol^{-1} s^{-1} and k_1/k_{-1} = 6.2 for $H_3PW_{12}O_{40}$ at 110 °C.[167] Since the HPA are weak acids in solution in acetic acid ($pK_1 \cong 5$),[41] the first order term in HPA shows that the reaction proceeds via general acid catalysis by undissociated HPA molecules. The catalytic activity of the HPA is almost independent of their composition and is ~100 times higher than the activity of H_2SO_4, which agrees well with the dissociation constants of the acids in acetic acid (Table 1). In the course of reaction (28), the HPA-Mo are appreciably reduced and for this reason their values of k_1 are lower than for the HPA-W.

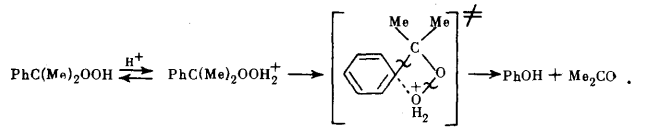
2. The Composition of Alkylphenyl Hydroperoxides

This important reaction constitutes the basis of the industrial method of the joint synthesis of phenol and acetone. It is catalysed by many HPA-Mo and HPA-W:[129,168,169]

$$PhC(Me)_2OOH \xrightarrow[40\rightarrow90\,^\circ C]{HPA} PhOH + Me_2CO . \quad (29)$$

Reaction (29) proceeds with a quantitative yield in solution in acetone or in an equimolar mixture of phenol and acetone for [HPA] = 0.01–0.08 wt.%. The selectivity of the HPA is so high that the phenol obtained does not require purification before its subsequent hydrogenation to cyclohexanol in the presence of the palladium catalyst[168].

The acid decomposition of alkylphenyl hydroperoxides proceeds via the protonation of the peroxy-group and subsequent synchronous rearrangement in the cyclic transition state (see Kozhevnikov and Kulikov[128] and the references quoted therein):



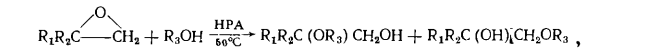
Reaction (29) in acetone in the presence of $H_3PMo_{12}O_{40}$ proceeds via the mechanism of general acid catalysis:

$$w = (k_H[H^+] + k_A[H_3PMo_{12}O_{40}^-])[ROOH] .$$

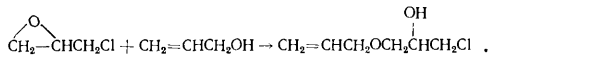
$k_H = 4.5$ litre mol^{-1} s^{-1} and $k_A = 14$ litre mol^{-1} s^{-1} were obtained at 25 °C.[129] Under the conditions indicated, the acid $H_2PMo_{12}O_{40}$ has a fully dissociated first proton and partly the second proton[40]. The main contribution comes from the $k_H[H^+]$ specific acid catalytic pathway. The catalytic activity of the HPA in acetone varies in parallel with their dissociation constants and is higher by a factor of 10^3 than the activity of H_2SO_4. HPA on γ-Al_2O_3 also catalyse reaction (29), but the activity of the heterogeneous catalyst is much lower than that of the homogeneous catalyst[129].

3. Other Reactions of the Acid Type

The acids PW_{12}, PMo_{12}, and SiW_{12} are effective homogeneous catalysts of the alcoholysis of epoxides with formation of hydroxyethers:

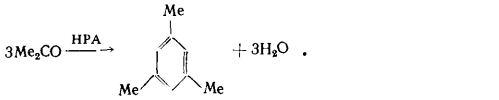


where R_{1-3} = H, alkyl, or aryl[170]. In the presence of an excess of the alcohol the polymerisation of epoxides does not take place. On interaction with allyl alcohol, epichlorohydrin gives rise to 1-allyloxy-3-chloro-2-propanol in 95–97% yield:



The reaction is of first order with respect to epichlorohydrin and the HPA. The strongest acid PW_{12} is also the most active catalyst among the HPA investigated; H_2SO_4 and $HClO_4$ are less effective than the HPA.

The acids $H_{8-x}X^xM_{12}O_{40}$ (X = Si^{VI} or P^V; M = Mo^{VI} or W^{VI}) on a solid carrier or in solution catalyse the condensation of alkyl ketones to aromatic compounds[171,172]. In the presence of a heterogeneous catalyst, the reaction requires severe conditions (200–450 °C, 7×10^3 kPa).[171] The homogeneous condensation proceeds under milder conditions. Thus in a solution of 40 wt.% HPA in acetone at 25 °C, aromatic hydrocarbons (mesitylene and other alkylbenzenes) are obtained at 25 °C in the course of 1–10 days in 40–55% yield relative to the reacted ketone in a mixture with water, methyl acetate and mesityl oxide[172]:



The degree of conversion of acetone is 25–45% and the catalyst can be used repeatedly.

In the presence of the HPA as homogeneous or heterogeneous acid catalysts, other reactions of practical importance also take place, such as the alkylation of aromatic compounds by olefins[173], the carbonylation of alcohols, the synthesis of formic acid from CO and water[174], the oligomerisation of olefins[175], etc.

V. APPLICATIONS OF HETEROPOLYACIDS IN HETEROGENEOUS CATALYSIS

Heteropolyacids and their salts have been used for a long time as heterogeneous catalysts in various oxidative and acid processes of practical importance. The studies up to 1975 have been briefly considered in a number of reviews[7,10,15]. It has recently become clear that heteropolycompounds are also of great interest for fundamental research into heterogeneous catalysis[2,176]. By altering the composition of the HPA, it is possible to vary independently and within wide limits their oxidising and acidic properties and also to achieve bifunctional catalysis. The constancy of the structure and the similarity of many physicochemical properties of the HPA in crystals and in solution (see below) permit the employment of the ideas concerning the mechanism of homogeneous catalytic reactions of the HPA for the analogous heterogeneous catalytic reactions.

HPA hydrates in the form of massive specimens are usually employed in heterogeneous catalysis. They are frequently deposited (10–15 wt.%) on solid carriers (SiO_2, Al_2O_3, etc.). Many HPA exhibit a fairly high thermal stability. For example, the acids PW_{12}, SiW_{12}, PMo_{12}, and $SiMo_{12}$ have average decomposition temperatures of 465°, 445°, 375°, and 350 °C respectively[107]. It is significant that the thermal stability of the HPA greatly increases in the presence of water vapour[177], but there are few quantitative data concerning this question.

The HPA hydrates behave in many respects similarly to solutions, which enables one to expect an analogy between the mechanisms of the action of the homogeneous and heterogeneous HPA-based catalysts. The behaviour of the HPA as a "pseudoliquid phase" [176] is manifested primarily in the mobility of structural elements. In the HPA hydrates, the polyanions are not linked to one another; the regularity of the packing is achieved as a result of the formation of hydrogen bonds with the molecules of the water of crystallisation[9,10]. According to ^{31}P NMR data, in the PW_{12} and PMo_{12} acid hydrates with a high water content the heteropolyanions rotate fairly readily at a frequency $\geq 10^3$ Hz [178] and their acid protons exchange rapidly with the protons of the water of crystallisation[73,74,105,106]. Even in anhydrous HPA the structural elements migrate freely at temperatures in excess of 150 °C. The activation energy for the self diffusion of H^+ decreases with increasing acid strength and amounts to 78.5, 54.6, 44.1, and 29.4 kJ mol^{-1} for PW_{12}, SiW_{12}, PMo_{12}, and $SiMo_{12}$ respectively. Small amounts of added water vapour accelerate the self diffusion of H^+.[107] The oxygen atoms in the M=O and M–O–M bonds in crystalline HPA exchange with water, as in solutions[176]. The rate of exchange of oxygen in the HPA is appreciably higher than in metal oxides. Thus 80% of the oxygen in PMo_{12} is exchanged in the course of 1 h at 250 °C, while only 0.4% is exchanged in MoO_3 in the course of 1.5 h at 440 °C.[176]

The adsorption of pyridine on massive specimens of the HPA PMo_{12}, PW_{12}, and $SiMo_{12}$ has been studied[176,177]. It has been established that the entire adsorbed pyridine exists in the form of the ion $C_5H_5NH^+$, i.e. the acidity of the HPA is of the Brønsted type. The amount of pyridine per HPA molecule is equal to the basicity of the HPA and is independent of the fact that part of the heteropolyanion is inaccessible to pyridine vapour. Thus not only surface

protons but also protons belonging to the heteropolyanion and located within the bulk of the specimen react with pyridine, similarly to reactions in solution[176]. The acidity of the crystalline HPA has been little investigated; according to the available data[107,176], the acidities of the HPA in the solid state and in solutions vary equally with their composition.

At 200–250 °C, $H_3PMo_{12}O_{40}$ is reduced by hydrogen. On subsequent treatment with molecular oxygen, the reduced form is reoxidised to the initial state. Such oxidation-reduction transformations of PMo_{12} are fully reversible for the addition (in the reduction process) of two electrons by an HPA molecule, but become irreversible when the degree of reduction corresponds to the addition of five electrons[176]. The analogy between the oxidation-reduction properties of solid HPA and the properties of the HPA-*n* in solutions can be seen in this example (see Section III).

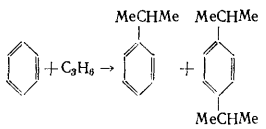
There have been several new studies of the application of the HPA in heterogeneous acid and oxidative catalysis and of the mechanism of their catalytic action. Like zeolites, the HPA-W catalyse the conversion of methanol into hydrocarbons[179]. Such reactions are of great interest in connection with the problem of the synthesis of an artificial liquid fuel from CO and H_2. In the presence of PW_{12} in a flow-type reactor at 245–357 °C and at atmospheric pressure, a mixture of olefins and alkanes ranging from C_1 to C_7 as well as traces of CO and CO_2 are formed. At 245 °C the mixture contains 43% of the butane–butene and 27% of the pentane–pentene fractions. The selectivity with respect to these products decreases with increase of temperature. A mechanism analogous to that of the corresponding reactions in the presence of superacids in solution has been proposed:

$$MeOH + H^+ \rightarrow Me^+ + H_2O\ ,$$

$$Me^+ + MeOH \rightarrow \left[\begin{matrix} H \\ Me^+ \end{matrix}\right\rangle\!\cdots CH_2OH \rightarrow MeCH_2OH + H^+\ ;$$

$$MeCH_2OH \rightarrow C_2H_4 + H_2O\ .$$

The very active catalyst of the alkylation of benzene by propene (the first stage of the cumene process of the synthesis of phenol and acetone) is 40% $H_4SiW_{12}O_{40}/SiO_2$:[173]



(30)

The reaction proceeds at 150 °C, 15×10^2 kPa, and $[C_6H_6]/.[C_3H_6] = 4$ with a selectivity of 72.5% with respect to isopropylbenzene for a propene conversion of 97.5%. The lifetime of the catalyst is 500 h. Di-isopropylbenzene is returned to the system to be transalkylated. The SiW_{12} HPA has virtually the same parameters as the aluminosilicate catalyst—one of the best heterogeneous catalysts of reaction (30). However, the latter operates under more severe conditions (300 °C and 3×10^3 kPa). In the alkylation process the catalysts are gradually saturated with coke and require regeneration; the coke is burnt off in a stream of air. After regeneration, the aluminosilicate catalyst has the previous activity and stability, but the HPA does not withstand severe regeneration conditions—it is dehydrated and loses activity irreversibly. This example demonstrates the urgent need for the development of new methods of regenerating HPA-based catalysts which do not reduce their activity.

The kinetics of the dehydration of isopropyl alcohol in the presence of HPA have been studied by a flow method[176]. The steady-state rate of reaction at 100 °C, referred to the catalyst surface, decreases in the following sequence of HPA: $PW_{12} > SiW_{12} > PW_{10}V_2 > PMo_{12} > PMo_{10}V_2 \cong SiMo_{12}$, and in the following sequence of their salts: $H_3PW_{12}O_{40} > Na_2.HPW_{12}O_{40} > Na_3PW_{12}O_{40}$. The catalytic activity of the HPA is satisfactorily correlated with their dissociation constants in acetone (Table 1).

The mechanism of the oxidation of methacrolein (RCHO) to methacrylic acid has been investigated in the presence of water vapour ($p_{H_2O} \cong 40$ kPa) at 280–300 °C.[176] The catalysts were massive HPA and their salts. The HPA-Mo (PMo_{12}, $SiMo_{12}$) and their copper(II) and caesium salts proved to be the most active and selective. The tungsten(VI) compounds have a lower activity and selectivity. In a flow reactor at 300 °C in the presence of PMo_{12} the reaction proceeds with a selectivity of 74.4% and a conversion of the substrate of 16.6%. Acetic acid (2.3%), Co (11.9%), and CO_2 (11.4%) are also formed. Water plays an important role in this reaction: in the absence of water, the selectivity and conversion are much lower. The process proceeds in accordance with the kinetic equation

$$-d[RCHO]/d\tau = kp_{RCHO}^{(0.8-1.0)}p_{O_2}^{(0.6-0.2)}p_{H_2O}^{0}\ . \qquad (31)$$

The process selectivity hardly changes after the cessation of the supply of O_2 under the conditions of the steady-state activity of the catalyst, which shows that the reaction proceeds in accordance with the oxidation-reduction mechanism via the following stages:

$$RCHO + HPA + H_2O \rightarrow RCOOH + H_2(HPA); \qquad (32)$$

$$H_2(HPA) + \tfrac{1}{2}O_2 \rightarrow HPA + H_2O\ . \qquad (33)$$

It follows from the kinetic equation(31) that stage (32) is rate-limiting. The mechanism described by reactions (32) and (33) is also supported by the rapid exchange of ^{18}O between acroleine and PMo_{12} at 300 °C.[176]

In principle, using HPA it is possible to achieve bifunctional oxidative and acid catalysis, but this interesting application of the HPA has so far been only slightly investigated. It has been established that, together with the oxidative properties of the HPA, their acidity plays a significant role in the oxidation of methacroleine, which has been confirmed by the poisoning of the catalyst by added pyridine[176]. The bifunctional catalysis by the HPA probably occurs in the oxidative hydration of propene to acetone[180].

Among new and promising but hitherto little investigated applications of HPA in heterogeneous catalysts, one should mention their employment for the synthesis of catalysts having a specified composition. All or some of the components of the catalyst can then be incorporated in the heteropolycomplex as ligands, central atoms, or outer-sphere cations. The complex is then deposited on a carrier and is subjected to a chemical or thermal treatment in order to obtain the final catalyst. This method has significant advantages over the successive deposition of the components. It reduces the number of stages in the preparation of the catalyst and ensures a very intimate mixing of the components (up to mixtures at the molecular level) starting from the heteropolycomplex, which is much more difficult and sometimes impossible to achieve by other methods. Studies[181,182] in which the formation of HPA on the surface of a solid carrier during the synthesis of heterogeneous catalysts by traditional methods was observed are of interest in this connection. Thus the silica–molybdenum oxide catalyst for the oxidation of propene, obtained by the spray drying of an aerosil suspension in an ammonium paramolybdate solution, contains molybdosilicic acid which determines the activity of the catalyst in the oxidation of propene. The HPA obtained in stable up to 500–600 °C as a result of stabilisation by the SiO_2 surface.

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Polycyclic Azulenoid Systems

Yu.N.Porshnev, V.B.Mochalin, and M.I.Cherkashin

The principal methods of synthesis of polycyclic azulene hydrocarbons and their derivatives are described and certain aspects of the practical applications of polycyclic azulenes are considered.
The bibliography includes 122 references.

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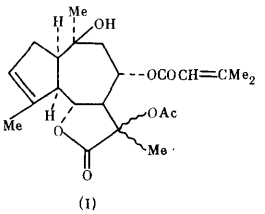
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I. INTRODUCTION

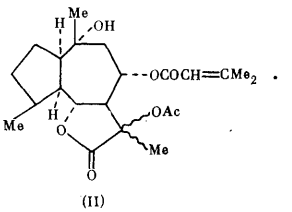
Azulene derivatives containing more than two condensed rings in the molecule have come to be called polycyclic azulenes. At the present time several tens of polycyclic azulenoid systems containing from three to seven condensed rings are known, many derivatives incorporating nitrogen-, sulphur-, and oxygen-containing heterocycles. To facilitate the description and nomenclature of polycyclic azulenes, we divided them into two subgroups: (1) carbocyclic azulenoid systems; (2) azulenes condensed with nitrogen-, sulphur-, and oxygen-containing heterocycles. The true heterocyclic analogues of azulenes as well as their π-electronic analogues—the so-called pseudoazulenes containing heteroatoms directly in one or both rings of the pseudoazulene nucleus—are not considered in this review because their number is very large and they might constitute the subject of a special review (see, for example, Timpe and Elcov[1]).

It is noteworthy that fully conjugated, i.e. dehydrogenated, polycyclic azulene hydrocarbons are not encountered in nature.

Only sesquiterpene precursors of polycyclic azulenes, usually incorporating saturated oxygen-containing heterocycles of the lactone type, are known. For example, the sesquiterpene derivatives (I) and (II) have been isolated from the extract of the roots of *Laserpitium silver*:

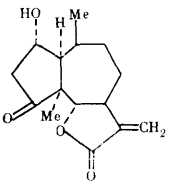


(I)

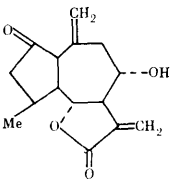


(II)

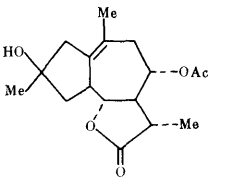
The structure of ivoxanthin (III)—a sesquiterpene lactone isolated from *Cyclachaena xanthifolia*[3], grossheimin (IV), isolated from *Grossheimia macrocephala*[4], and certain other sesquiterpenes [(V)–(VIII)] [5,6] which are in the main genetic precursors of guaiazulene and vetivazulene, have been established:



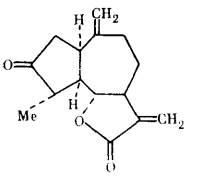
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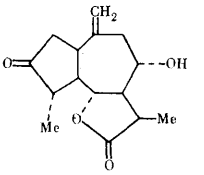
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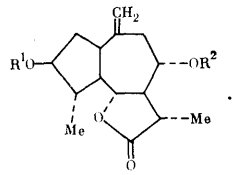
(V)



(VI)

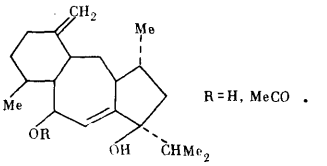


(VII)



(VIII)

The diterpene dolatriol (IX), which has the hydrocarbon skeleton of a hydrogenated precursor of 5,6-benzazulene, has been recently isolated from the tissues of molluscs[7]. Its structure was established by X-ray diffraction:



(IX)

The majority of carbocyclic azulenes have been considered[8] in connection with the discussion of a new approach to the concept of the aromaticity of conjugated cyclic hydrocarbons. The author bases his views on the concept of conjugated circuits recognised at the present time as significant structural elements characterising conjugated systems. The structures of conjugated hydrocarbons were investigated and circuits with an alternation of double and single C–C bonds were enumerated. Systems having only conjugated circuits of the $(4n + 2)$ type are defined as aromatic. Systems with conjugation contours only of the $(4n)$ type are regarded as antiaromatic, i.e. destabilised as a result of the delocalisation of the π electrons. Finally systems having circuits of both

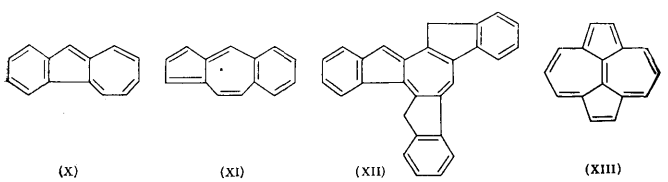
types simultaneously are classified as intermediate, manifesting only a partial aromatic character. This approach constitutes a logical extension to polycyclic systems of the famous Hückel (4*n* + 2) rule, which is rigorously applicable only to monocyclic systems. Furthermore, in the above study a brief comparison was made with several alternative schemes and their limitations were demonstrated[8].

Almost all polycyclic azulenes (particularly fully conjugated compounds) are high-melting readily crystallisable aromatic compounds. They are deeply coloured and frequently absorb light at longer wavelengths than the usual azulenes and their homologues and sometimes even in the near infrared. Isolated information concerning the synthesis of polycyclic azulenes is given in a number of reviews[9–11], but they do not provide a complete view of the state of affairs in this field, since they are devoted mainly to individual questions of synthesis or reactivity.

CARBOCYCLIC AZULENE DERIVATIVES

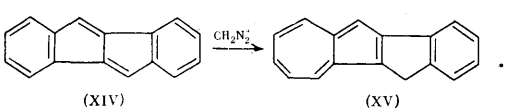
1. Expansion of the Benzene Ring of Azulene Precursors by Carbenes

The simplest tricyclic derivatives, namely the benzazulenes (X) and (XI), which are formed by the expansion of the benzene ring of fluorene and the corresponding indan derivative on treatment with an alkoxycarbonylcarbene, produced in its turn on thermal or catalytic decomposition of diazoacetic ester (the Buchner synthesis) with subsequent dehydrogenation and removal of the alkoxycarbonyl group, were obtained before other representatives of carbocyclic condensed systems[12–14].



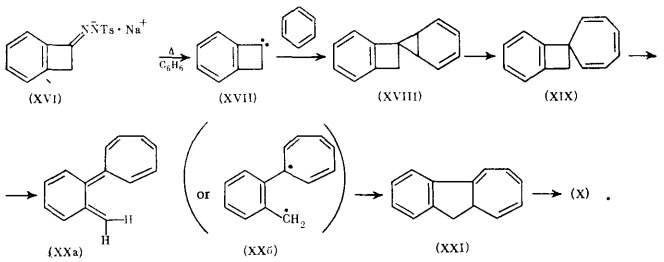
(X) (XI) (XII) (XIII)

Substituted 1,2-benzazulenes[15–18] as well as the heptacyclic azulene (XII)[19] and azupyrene (XIII),[20] which consists of a system of two condensed azulene nuclei, have been obtained analogously. The expansion of one of the benzene rings in 1,2 : 4,5-dibenzopentalene (XIV) leads to indeno[2,1-*a*]-azulene (XV):[21]



(XIV) (XV)

It has been shown recently that the thermolysis of the sodium salt of the tosylhydrazone of benzocyclobutenone (XVI) (a familiar method of synthesising carbenes[22]) in benzene gives rise to 9a,10-dihydrobenzo[*a*]azulene (XXI) in 30% yield. The synthesis of compound (XXI) can be represented as a result of the addition of benzocyclobutenylidene (XVII) to benzene with formation of spiro-norcaradiene (XVIII), which isomerises to spiro-cycloheptatriene (XIX). The ring opening of the benzocyclobutene part of compound (XIX) can lead to the *o*-quinodimethane derivatives (XXa) or to the equivalent biradical (XXb), which cyclises to compound (XIX). The dehydrogenation of compound (XXI) leads to benzo[*a*]azulene (X):[23]

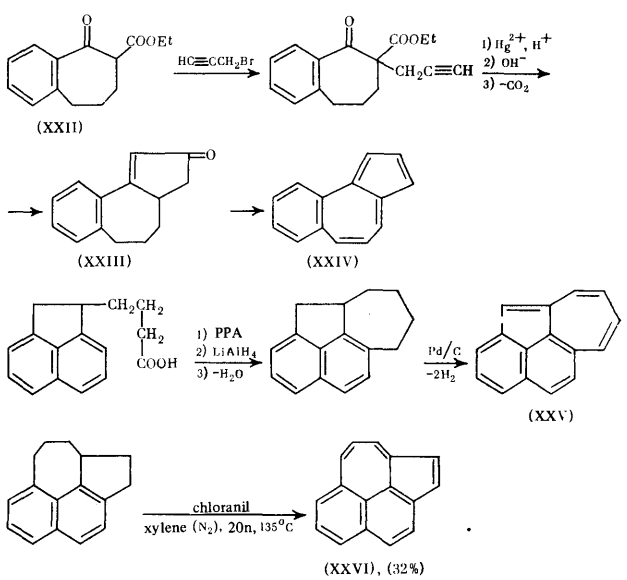


The methods described above are of great theoretical interest from the standpoint of the synthesis and study of new condensed azulenoid systems, but their preparative values is restricted by the low availability of the initial compounds and also by the low yields in the stages involving the expansion of the benzene ring and the dehydrogenation of the resulting precursors of azulene hydrocarbons. These methods have been significantly supplemented by syntheses which are based on the employment of non-azulenoid compounds as the starting materials, i.e. by another variety of the total synthesis.

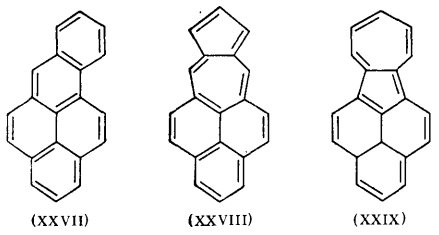
2. Total Synthesis of Carbocylic Derivatives of Azulene from Non-azulenoid Compounds

The total synthesis of polycyclic azulenes presupposes either the addition of a new five-membered ring to the complete seven-membered ring or conversely, at least one of the initial compounds must be condensed with at least one polymethylene, benzene, naphthalene, or another ring. The concluding stage is usually dehydrogenation.

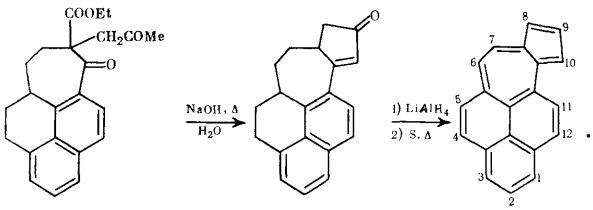
This method of synthesis of complex tri- and tetra-cyclic systems can be illustrated by the synthesis of 4,5-benzazulene (XXIV),[24] naphth[2,1,9,8-*ija*]azulene (XXV),[25] naphth[2,1,9,8-*cde*]azulene (XXVI),[26] and certain other derivatives:



In order to investigate the biological properties of polycyclic arenes and to compare them with the carcinogenic benzo[*a*]pyrene (XXVII), its non-alternant isomers were obtained: azuleno[5,6,7-*cd*]phenalene (XXVIII),[27] which exhibits a powerful carcinogenic activity, the weakly carcinogenic azulene[1,2,3-*cd*]phenalene (XXIX),[28] and azuleno-[4,5,6-*cd*]phenalene (XXX),[29] which, judging from the topology of its π-electron system [similarity to compound (XXVIII)] and its molecular structure [similarity to compound (XXVII)], should exhibit an appreciable biological activity:

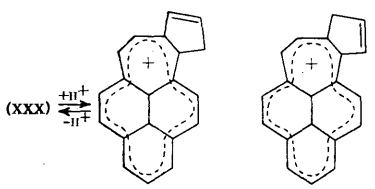


(XXVII) (XXVIII) (XXIX)



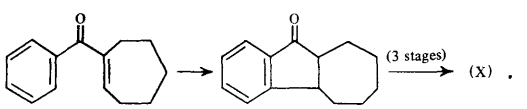
(XXX)

Compound (XXX) is distinctly basic and undergoes reversible protonation by trifluoroacetic acid, giving rise to a mixture of the cations (XXXIa) and (XXXIb) in proportions of 4 : 1:

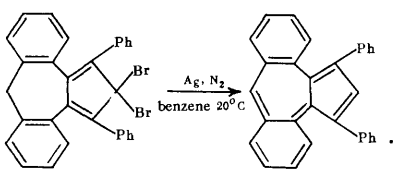


(XXXIa) (XXXIb)

An example of another method of closure of the five-membered ring is provided by the synthesis of 1,2-benzazulene [30–32]:

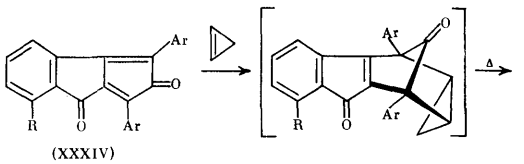


The synthesis of 1,3-diphenyldibenz[*eh*]azulene (XXXIII) by the dehydrobromination of the dibromo-derivative (XXXII) with silver dust in a nitrogen atmosphere was reported in 1974.[33] Compound (XXXIII) is stable only at temperatures not exceeding −18 °C (in a N_2 atmosphere).

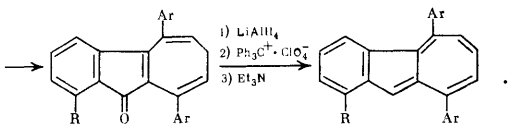


(XXXII) (XXXIII)

The synthesis of substituted 1,2-benzazulenes from the "indanocyclone" (XXXIV) was included among those which involve the rearrangement of the five-membered ring to a seven-membered ring with subsequent reduction and dehydrogenation of the intermediates[34]:



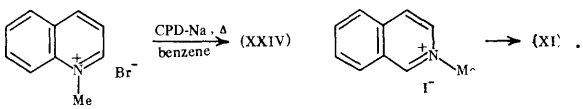
(XXXIV)



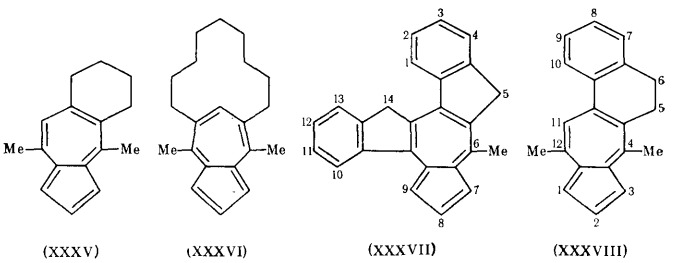
The methods examined have the advantage over those involving the expansion of the benzene ring in that they lead to final products with higher overall yields. However, they too are fairly cumbersome which reduces their preparative value compared with methods based on the cleavage of certain heterocyclic systems.

3. Quinolinium, Isoquinolinium, and Pyrylium Salts in the Synthesis of Polycyclic Azulenes

In contrast to pyridinium salts, quaternary quinolinium[35] and isoquinolinium[36] salts give rise to the corresponding benzazulenes (XXIV) and (XI) only in low yields on high-temperature condensation with cyclopentadienylsodium (CPD-Na):



There are at present almost no publications about the successful synthesis of polycyclic azulenes from benzopyrylium, isobenzopyrylium, and other condensed pyrylium derivatives. It is only known that tetrahydrobenz[*f*]azulene (XXXV) has been obtained from a tetrahydrobenzopyrylium salt and cyclopentadienylsodium is 3.3% yield[36] and that 4,8-dimethyl-5,7-nonamethyleneazulene (XXXVI) has been synthesised from the corresponding salt in 0.3% yield[37].



(XXXV) (XXXVI) (XXXVII) (XXXVIII)

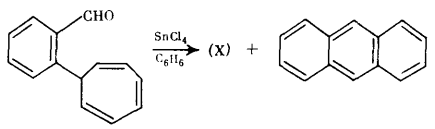
The deficiencies of the above syntheses are extremely low yields and the low availability of the initial salts, for example, in the second case. However, despite the fact that the methods have been as yet hardly elaborated, their possibilities are probably very considerable. It has been established recently that 2-methyldi-indeno[2,3;2',3'-*c*;*e*]pyrylium perchlorate, obtained by the method of Zhdanov et al.[38], reacts

with cyclopentadienylsodium to form 6-methyldi-indeno[3,2;;3',2'-*e*;*g*]azulene (XXXVIII) in 16% yield[39]. Under similar conditions, 2,10-dimethyl-3,4-dihydronaphtho[2,1-*c*]pyrylium perchlorate[40] gives rise to 4,12-dimethyl-5,6-dihydronaphth-[2,1-*f*]azulene (XXXVIII) in 22% yield[39]. The attempt to dehydrogenate compound (XXXVIII) by chloranil led merely to the product of "*ene*-synthesis", as in the reaction of *p*-benzoquinone with azulene[41].

When the initial substance contains a complete unsaturated seven-membered ring, the possibilities of the synthesis are greatly expanded. Such initial compounds may be, for example, derivatives of the cycloheptatriene and cycloheptafulvene series.

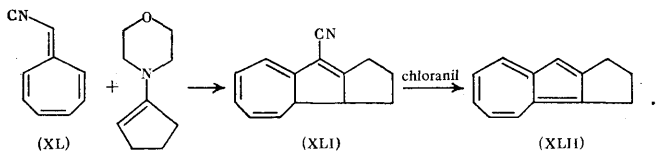
4. Syntheses based on Cycloheptatriene and Cycloheptafulvene Derivatives

Japanese investigators developed several methods for the synthesis of the five-membered ring of the azulene system from derivatives of the cycloheptatriene series, which lead to the formation of tri- and tetra-cyclic hydrocarbons. Thus, the catalytic intramolecular cyclisation of *o*-cycloheptatrienylbenzaldehyde (XXXIX) on treatment with $SnCl_4$ in benzene, leading to the formation of 1,2-benzazulene and anthracene, has been reported[42]:



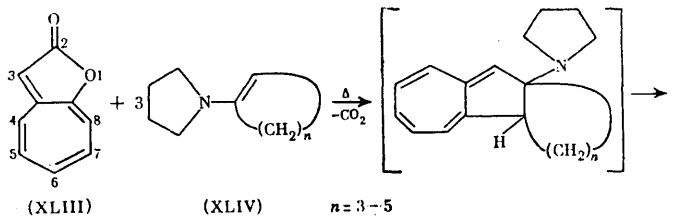
(XXXIX)

The condensation of 8-cyanocycloheptafulvene (XL) with morpholinocyclopentene leads to the formation of the dihydroazulene derivative (XLI), whose dehydrogenation yields 1-cyano-2,3-trimethyleneazulene (XLII):[43]

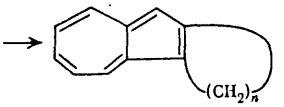


(XL) (XLI) (XLII)

It has been established[44] that 2*H*-cyclohepta[*b*]furan-2-one (XLIII), formed on condensation of equimolar amounts of 2-chlorotropone with sodiomalonic ester, also undergoes the cycloaddition reaction with enamines of type (XLIV) accompanied by the elimination of CO_2 and the amine, which leads to the formation of azulene derivatives (XLV):

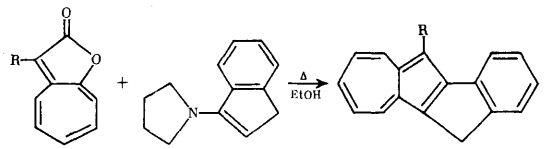


(XLIII) (XLIV) $n = 3-5$



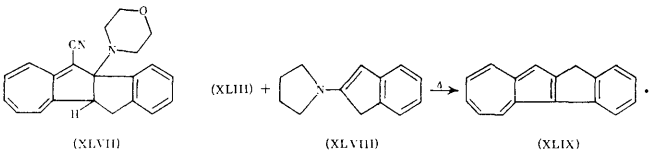
(XLV)

Heating of compound (XLIII), or its 3-cyano-derivative with 1-*N*-pyrrolidinoindene gives rise to indeno[2,1-*e*]azulene (XLVIa) or cyanoazulene (XLVIb) (yields 93 or 19% respectively):[45]



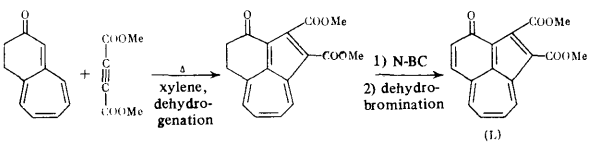
R = H (a), CN (b) (XLVI, a and b)

1-*N*-Morpholinoindene reacts with 3-cyano-2*H*-cyclohepta-[*b*]furan-2-one, forming 20% of compound (XLVIb) and 57% of the adduct (XLVII), which is converted quantitatively into compound (XLVIb) during chromatography on silica gel (eluent—benzene). The furanone (XLIII) reacts with 2-*N*-pyrrolidinoindene (XLVIII) much more slowly (140 h, 78 °C, alcohol), giving a 30% yield of indeno[1,2-*a*]azulene (XLIX), but compound (XLVIII) does not react with 3-cyanofuranone:



(XLVII) (XLVIII) (XLIX)

It was found that cycloheptafulvene derivatives can undergo the cycloaddition reaction with strong dienophiles, which led to the formation of the new tricyclic fully conjugated 3-*H*-benzo[*cd*]azulenone (L) system[46]:



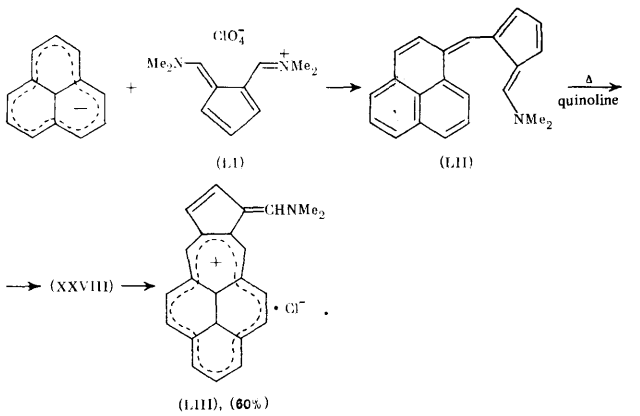
(L)

Presumably the scope for development of the above methods of synthesis may be inherent in the properties of the benzotropone and benzocycloheptafulvene derivatives (or other condensed systems of this type), but at the present time such data are not available.

5. Cyclisation of Polymethinium Salts and Fulvenes

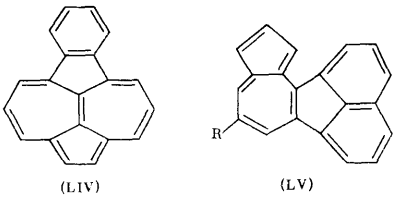
The cyclisation of fulvenes, developed by Ziegler and Hafner, is at present perhaps the most effective method of synthesis of azulenes[47,48]. This method proved to be effective also for the synthesis of polycyclic azulenes which are dfficult to obtain, such as, for example, azuleno[5,6,7-*cd*]-phenalene. The phenalene anion condenses with 6-dimethylamino-2-dimethylimmoniamethylfulvene perchlorate (LI) to form the enamine (LII), which can be converted into azuleno-[5,6,7-*cd*]phenalene by thermal cyclisation with elimination of dimethylamine[27]. Compound (XXVIII) is more basic than azulene and is extracted reversibly from benzene by 60%

H_3PO_4. When compound (XXVIII) is treated with the Vilsmeier reagent, the highly fluorescent salt (LIII) is formed:

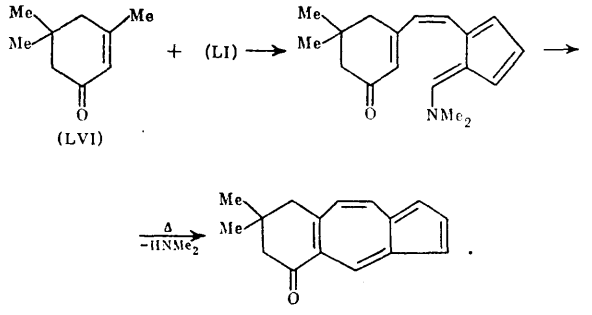


The carcinogenic azulene[5,6,7-*cd*]cyclopenta[*gh*]phenalene has been obtained similarly from the acephenalene anion[49].

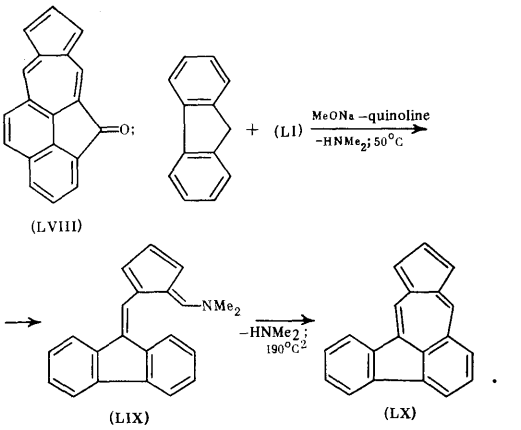
The cyclisation of fulvenes yielded azuleno[1,2,3-*cd*]-phenalene (XXIX) [28] and pyraceheptylene (XIII),[50] mentioned above, as well as benzopyraceheptylene (LIV) [50] and azuleno-[4,5-*a*]acenaphthylene (LV),[51] the mechanisms of the syntheses of which have been fully considered in a review[11].



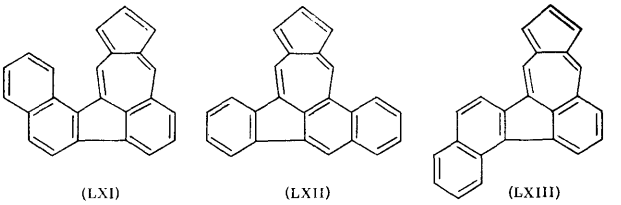
As in the synthesis of the azulene [5,6,7-*cd*]phenalene (XXVIII) system, the deprotonation of isophorone (LVI), in which the methyl group conjugated with the carbonyl group via the C=C bond reacts instead of the sterically hindered α-methylene group, leads to the formation of a stabilised allyl anion, which condenses with the heptamethinium salt (LI) to 7,7-dimethyl-5,6,7,8-tetrahydro[*f*]azulen-5-one (LVII) (yield 15%).[51]



Under similar conditions, 1-acenaphthenone condenses with compound (LI) to form a fulvenoid enaminoketone, which cyclises to azuleno[5,6,7-*cd*]acenaphthylen-6-one (LVIII) at 180 °C:[51]



The heptamethinium salt (LI) reacts similarly with fluorene to form the enamine (LIX), which undergoes ring closure at 190 °C to azuleno[5,6,7-*jk*]fluorene (LX) with elimination of dimethylamine. Benzofluorenes also condense with the salt (LXI), forming deeply coloured benzo-derivatives of the enamine (LIX), which can cyclise to the hexacyclic azulenes (LXI)–(LXIII). It has been established that only azulene-[5,6,7-*jk*]benzo[*a*]fluorene (LXI) is formed from benzo[*a*]-fluorene. However, the enamines formed from benzo[*b*]fluorene and benzo[*c*]fluorene can formally undergo ring closure via two different pathways, namely they can undergo annelation to the naphthalene or benzene nucleus of the benzofluorene system[51].



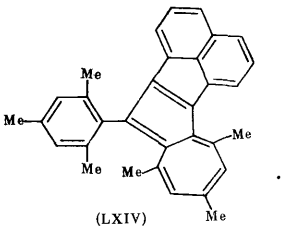
The azuleno[5,6,7-*jk*]benzo[*h*]fluorene (LXII) and azuleno-[5,6,7-*jk*]benzo[*c*]fluorene (LXIII) structures proposed by the authors[51] follow from the localisation energies L_r for the cyclisation reaction estimated by the Hückel method. In each case traces of the second isomer were detected. It is noteworthy that the theoretical evidence cannot replace, accordinto to the authors themselves, a rigorous chemical demonstration of structures (LXII) and (LXIII).

The cyclisation of polymethinium salts and fulvenes is one of the universal methods of synthesis of an extremely wide variety of highly condensed azulene hydrocarbons despite certain difficulties in the preparation of the initial and intermediate compounds. The scope of this method has been by no means fully exhausted, since, as will be shown below, other azulene derivatives readily enter into such reactions instead of fulvenes, cyclopentadienes, and other hydrocarbons.

6. Syntheses based on Acetylenic Compounds and Other Methods

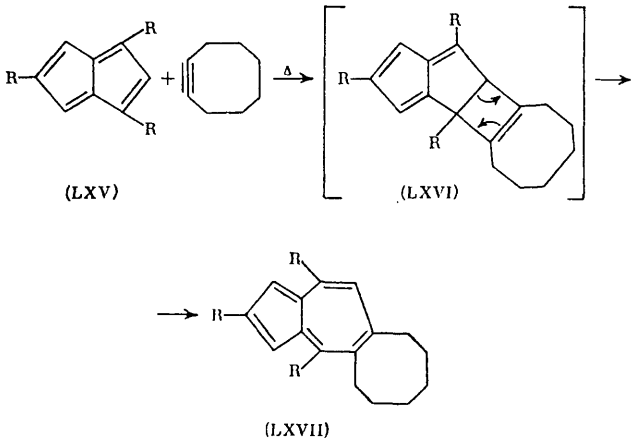
Among polycyclic fully conjugated azulenoid systems obtained from acetylene derivatives, only substituted acenaphthylenoazulene (LXIV), formed on irradiation of

diphenylperibisethynylnaphthalene, is known[52]:



(LXIV)

It has been observed[53] that the pentalene derivative (LXV) reacts at 270 °C with the highly strained triple bond of cyclo-octyne and it is tentatively suggested that this involves the intermediate formation of the cyclobutene derivative (LXVI), yielding 2,4,12-tri-t-butyl-5,6,7,8,9,10-hexahydrocyclo-octa[*f*]azulene (LXVII):

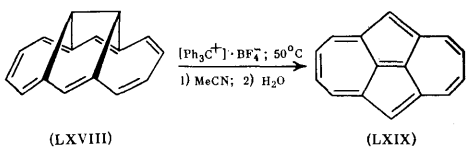


(LXV) (LXVI) (LXVII)

R = t-Bu .

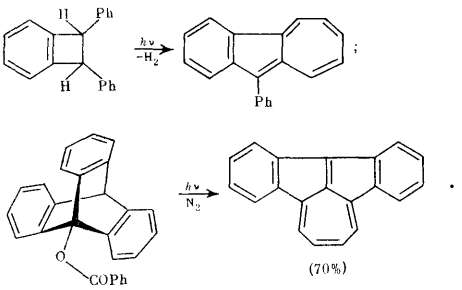
The exclusive formation of compound (LXVII) in 70% yield at such a high temperature indicates (in contrast to pentalene and methylpentalene) only a slight tendency of the 2,4,6-trisubstituted pentalene (LXV) to dimerise, i.e. the steric influence of bulky substituents.

An interesting reaction involves dehydrogenation of the non-polar 1,6,8,13-ethanediylidene[14]annulene (LXVIII) to dicyclohepta[*cd,gh*]pentalene (LXIX), which takes place under the influence of triphenylcarbonium tetrafluoroborate in 70% yield, has been discovered[54]. Compound (LXIX) is a new non-benzenoid isomer of pyrene:



(LXVIII) (LXIX)

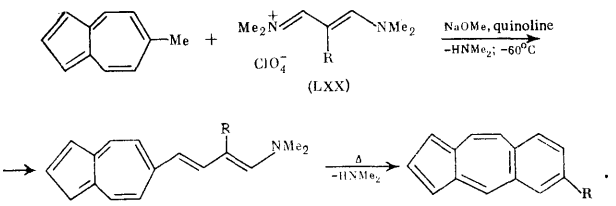
The photochemical isomerisation of 3,4-diphenyl-1,2-benzocyclobutene to 1-phenyl-2,3-benzazulene[55] and of benzoyloxytriptycene to benz[*a*]indeno[1,2,3-*cd*]azulene [56] has been described:



The fact that in the methods of synthesis described the azulene system is formed from the most "unexpected" precursors confirms its fairly high thermodynamic stability.

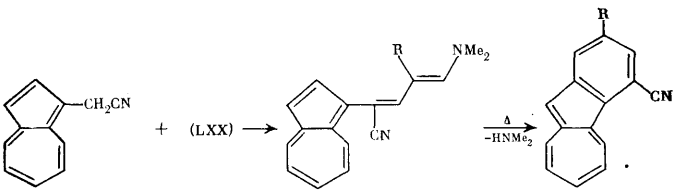
7. Derivatives of Azulenes as Starting Materials for the Synthesis of Polycyclic Systems

Many new and extremely varied polycyclic azulenoid systems have been obtained from comparatively simple azulene derivatives containing functional groups in the five-membered ring, seven-membered ring, or both rings simultaneously. The formation of the benzo-ring on the azulene system may be illustrated by the synthesis of 5,6-benzazulene and its derivatives[57]:



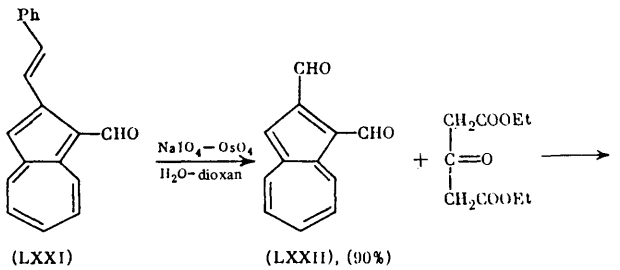
(LXX)

Here R = H, Et, Ph, $PhCH_2$, or OMe. The successful condensation of their trimethinium salt (LXXX) with the methyl group of 6-methylazulene is evidently due to the electron-accepting influence of the seven-membered ring of the azulene system, which leads to an increase of the mobility of the methyl protons. The authors[57] used the mobility of the methylene protons in 1-azulenylacetonitrile to achieve the formation of a similar 1,2-benzo-ring:

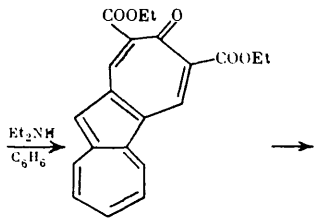


The corresponding functional derivatives of azulene, for example, 1,2-diformylazulene (LXXII), obtained[58] from 2-styrylazulene-1-aldehyde (LXXI) by the Lemieux–Johnson oxidation, are very convenient for the formation of new rings condensed with the 1- and 2-positions of the azulene nucleus. Subsequent condensation of the dialdehyde (LXXII) with acetonedicarboxylic ester, hydrolysis, and decarboxylation

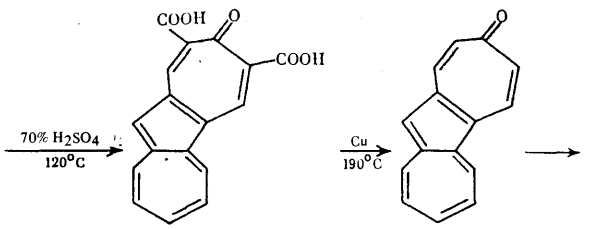
lead to azuleno[1,2-*d*]tropone (LXXIII):[58]



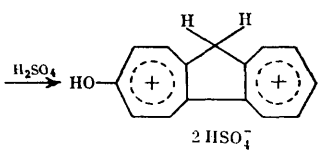
(LXXI) (LXXII), (90%)



(58%)



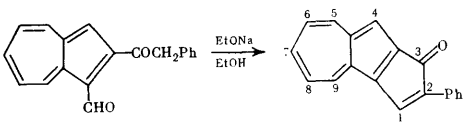
(LXXIII), (31%)



(LXXIV)

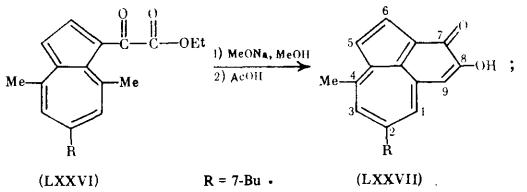
Azulenotropone (LXXIII) dissolves in H_2SO_4 with formation of the doubly charged cation (LXXIV).

Another example of the utilisation of a 1,2-dicarbonyl derivative of azulene is the synthesis of 2-phenylazuleno-[1,2-d]cyclopentadien-3-one (LXXV):[59]



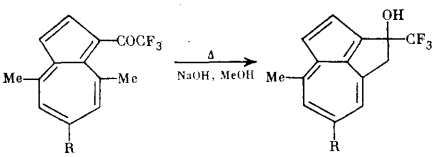
(LXXV).

In those compounds where the functional groups or substituents reacting with one another are located in different rings of the azulene system, for example, in the 1- and 8-positions, intramolecular condensation leads to a closer condensation of the newly formed ring with the azulene nucleus. Thus ethyl 6-t-butyl-4,8-dimethyl-1-azulenyl glyoxylate (LXXVI) cyclises to 2-t-butyl-8-hydroxy-4-methyl-7*H*-benz[*cd*]azulen-7-one (LXXVII) on treatment with sodium methoxide[60]:



(LXXVI) R = 7-Bu . (LXXVII)

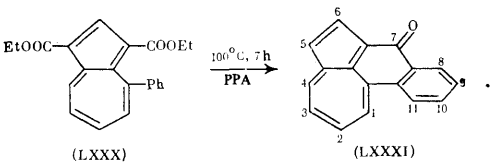
The analogous treatment of 1-trifluoroacetyl derivatives of 4,6,8-trimethylazulene (LXXVIIIa)[61] or 4,8-dimethyl-6-styrylazulene (LXXVIIIb)[39] results in the formation of the corresponding stable tertiary alcohols—derivatives of dihydroaceazulene (LXXIX, a and b):



(LXXVIII, a and b) (LXXIX, a and b)

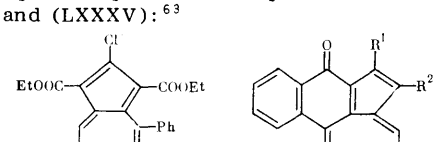
R = Me (a), —CH=CH—Ph (b) .

The intramolecular cyclisation of diethyl 4-phenylazulene-1,3-dicarboxylate (LXXX) has been achieved[62] in polyphosphoric acid (PPA) with formation of a new heterocyclic system—7*H*-naph[3,2,1-cd]azulen-7-one (LXXXI), which is the azulene analogue of benzanthrone:



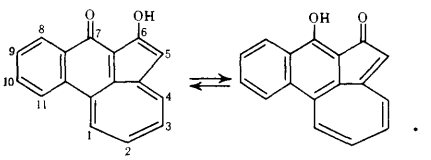
(LXXX) (LXXXI)

The cyclisation of the 2-chloro-derivative (LXXXII) at 100 °C for 3 h in polyphosphoric acid results in the formation of all three possible products—compounds (LXXXIII), (LXXIV), and (LXXXV):[63]



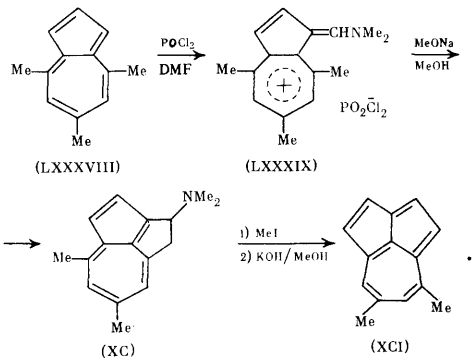
(LXXXII) (LXXXIII): R^1 = Cl, R^2 = H;
(LXXXIV): R^1 = Cl, R^2 = COOEt;
(LXXXV): R^1 = H, R^2 = COOEt .

The ethoxycarbonyl group can be eliminated from compound (LXXXIV) and the latter can exchange its chlorine for the methoxy-group: the demethylation of the intermediate methoxy-derivative yields 6-hydroxy-7*H*-naphth[3,2,1-*cd*]azulen-7-one (LXXXVI), which exists in tautomeric equilibrium with compound [LXXXVII]:



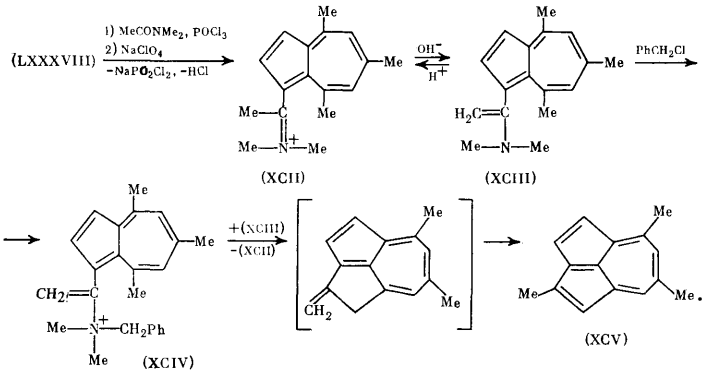
(LXXXVI) (LXXXVII)

The mobility of the hydrogen atoms in the methyl groups of 4,6,8-trimethylazulene enabled Hafner and Schneider[64] to achieve the closure of the five-membered ring condensed along the *cd* faces of the azulene nucleus, which ultimately led to the formation of a new tricyclic conjugated system—aceazulene (XCI):

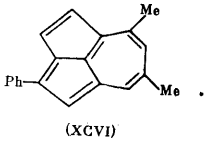


Like acenaphthylene, compound (XCI) is not aromatic; it is stable only at temperatures below 77 °C.

In the Vilsmeier acetylation of compound (LXXXVIII), the immonium salt (XCII) formed initially does not hydrolyse immediately to an acetyl derivative when rendered alkaline but gives rise to the enamine (XCIII). Treatment of the latter with benzyl chloride results in the intermediate formation of a quaternary ammonium salt (XCIV), which undergoes the Hofmann cleavage on treatment with an excess of the enamine (XCIII), accompanied by the closure of a new five-membered ring with formation of the aceazulene derivative (XCV):[65]

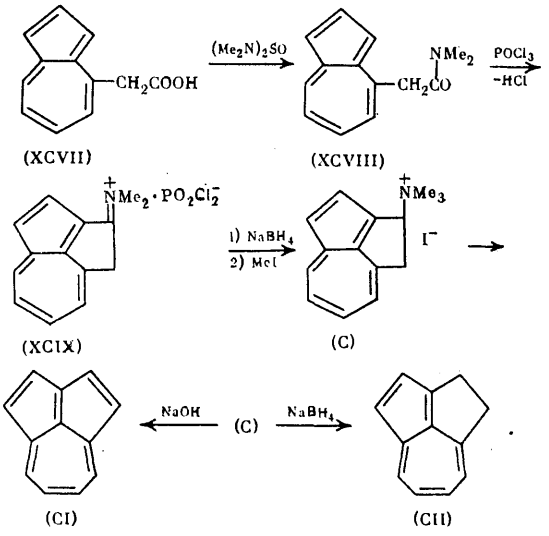


The Vilsmeier benzoylation of compound (LXXXVIII) also results in the formation of the corresponding aceazulene derivative (XCVI) in addition to the main reaction product (the 1-benzoyl derivative):

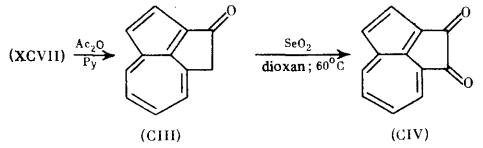


(XCVI)

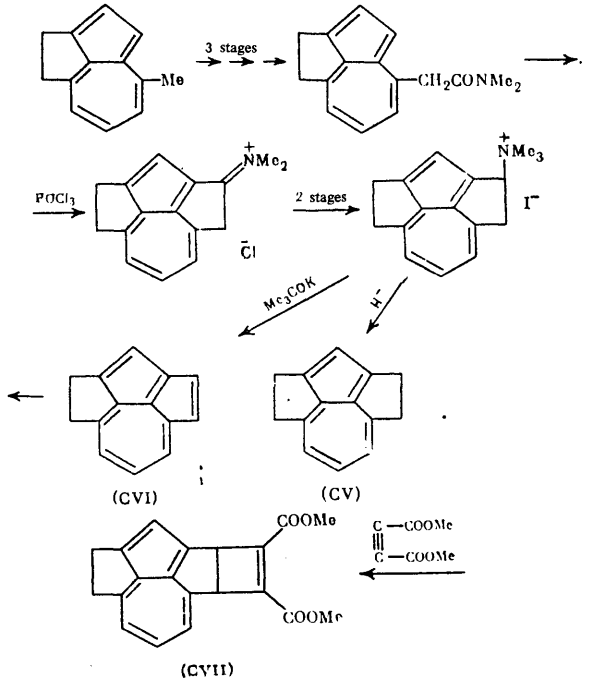
The unsubstituted cyclopent[*cd*]azulene (CI) was obtained from azulene-4-acetic acid (XCVII) as a result of a series of successive transformations[66]:



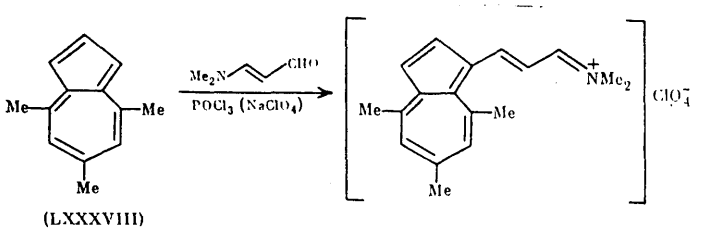
Direct cyclisation of compound (XCVII) in acetic anhydride in the presence of pyridine leads to the formation of the 2-oxo-derivative (CIII), whose oxidation with selenium dioxide in dioxan (60 °C, 3 h) yielded cyclopent[*cd*]azulene-1,2-dione (CIV)—a non-benzenoid isomer of acenaphthenequinone[66]:



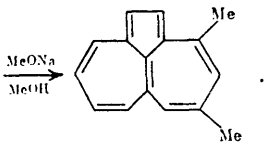
Using the scheme indicated below, Hafner et al.[66] obtained 1,2,6,7-tetrahydrodicyclopent[*cd;ij*]azulene (CV) and 1,2-dihydrodicyclopent[*cd;ij*]azulene (CVI); the latter is capable of undergoing the cycloaddition reaction with dimethyl acetylenedicarboxylate via one of the double bonds of the cyclopentane ring, forming the adduct (CVII):



Hafner and Schneider[64] obtained for the first time from 4,6,8-trimethylazulene (TMA) a new stable aromatic system—3,5-dimethylaceheptylene (CVIII):

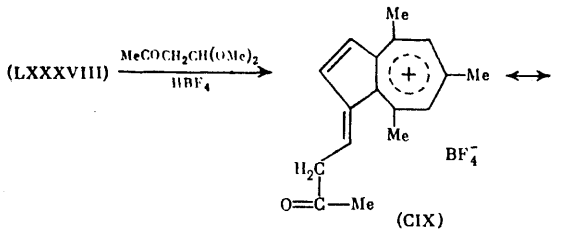


(LXXXVIII)

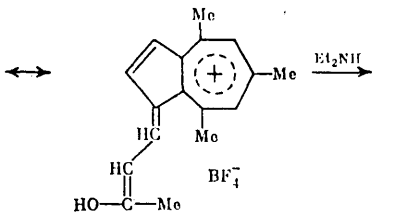


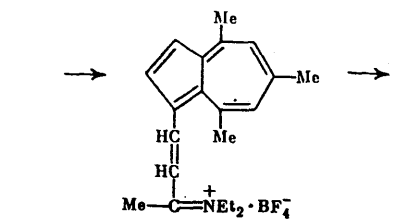
(CVIII)

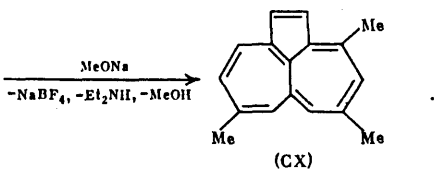
If formylacetone acetal in a strongly acid medium is used instead of β-dimethylaminoacroleine, then the intermediate azulenylium salt (CIX) is cleaved after treatment with diethylamine and subsequent heating with sodium ethoxide to form 3,5,8-trimethylaceheptylene (CX):[67]



(CIX)

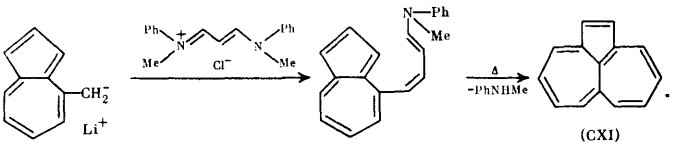






(CX)

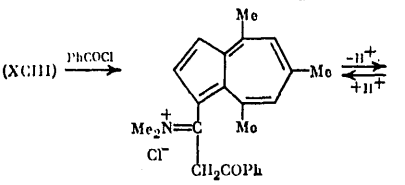
The unsubstituted aceheptylene (CXI) has been obtained by the intramolecular cyclisation of 1-(4-azulenyl)-4-methylphenylaminobutadiene[68]:

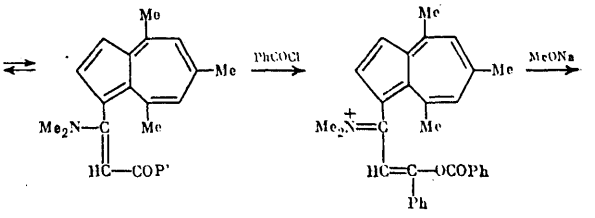


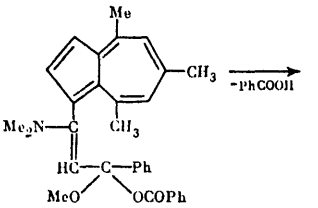
(CXI)

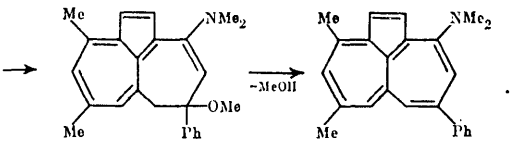
This method has been extended[57] to guaiazulene, from which a series of substitued aceheptylenes were obtained. Similar substituted derivatives have also been synthesised by the same workers from 4-methylazulene.

3,5-Dimethyl-10-dimethylamino-8-phenylaceheptylene (CXII) has been obtained by the benzoylation of the enamine (XCIII) in a series of successive stages[65]:



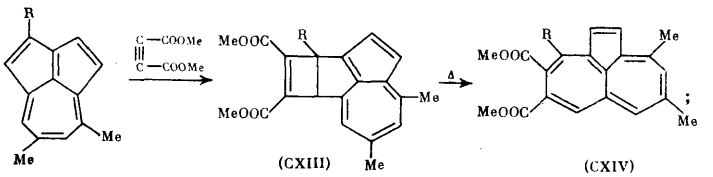






(CXII)

Derivatives of aceheptylene can be obtained also by the cycloaddition reaction of cyclopent[*cd*]azulenes with acetylenedicarboxylic esters followed by thermal isomerisation of the adduct (CXIV):[69]

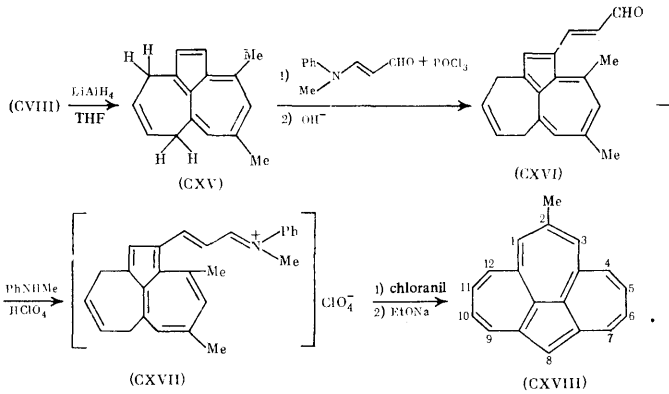


(CXIII) (CXIV)

R = H, Me, Ph .

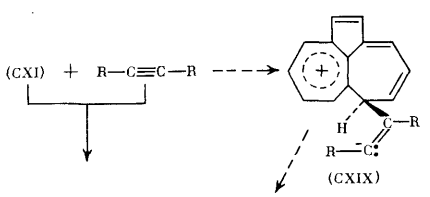
It has been established[70] that the aceheptylene derivative (CVIII) is reduced to the dihydro-derivative (CXV) on treatment with lithium tetrahydroaluminate. The involvement of

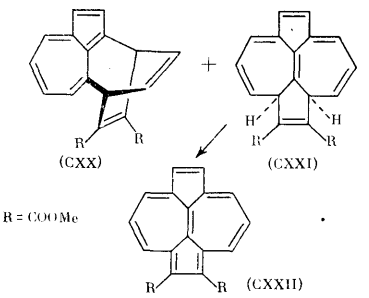
compound (CXV) in the Vilsmeier reaction ($POCl_3$ + β-methylphenylaminoacroleine) leads to the aldehyde (CXVI), which reacts with *N*-methylaniline in the presence of $HClO_4$ to form the immonium salt (CXVII). Dehydrogenation of the salt obtained with chloranil and subsequent cyclisation in the presence of bases lead to a new tetracyclic conjugated azulenoid system—2-methylazuleno[8,8a,1,2-*def*]heptalene (CXVIII):[70]



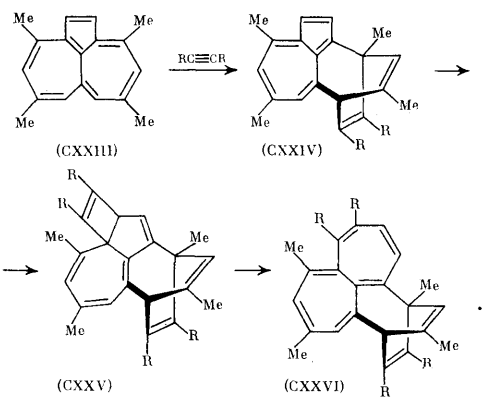
Pentalene[53], azulene, cyclopent[*cd*]azulene[71], and the readily available aceheptylene (CXI) [72] undergo cycloaddition reactions with activated alkynes unusually readily with formation of new polycyclic systems[73]. When compound (CXI) is heated for 1 h with dimethyl acetylenecarboxylate in 1 : 1 molar proportions in boiling tetralin, it is possible to obtain, together with the Diels–Alder adduct (CXX) (in 1% yield), also a 25% yield of 1,2-dicyclopenta[*ef*,*kl*]heptalenedicarboxylic ester (CXXII). The latter is probably formed from the primary adduct (CXXI), which can be obtained, like compound (CXX), from the intermediate dipolar compound (CXIX), arising either from the attack of the electron-accepting alkyne on the position with the highest electron density in the molecule of compound (CXI) or by virtue of a synchronous cycloaddition.

3,5-Dimethylaceheptylene and 3,5,8,10-tetramethylaceheptylene (CXXIII) react with acetylenic esters like compound (CXI).[70] However, in these cases the formation of a Diels–Alder adduct of type (CXX) predominates. The tetracyclic system on which compound (CXXII) is based had been obtained earlier only by a multistage procedure with an extremely low overall yield[74]. Within the limits of the possible comparison, the spectroscopic properties of compound (CXXII) are consistent with those of the unsubstituted tetracyclic hydrocarbon:



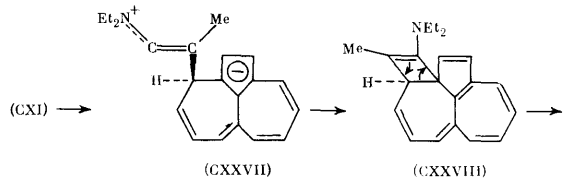


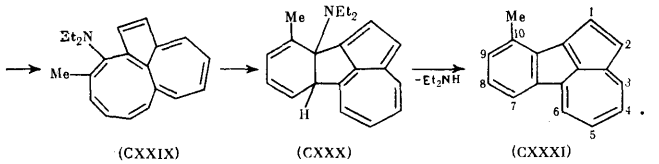
Like azulene, Diels–Alder adducts of type (CXX) undergo a dipolar cycloaddition reaction with acetylenedicarboxylic ester at 200 °C in the 1,8a-positions of the azulenoid component of compound (CXX). Thus, 3,5,8,10-tetramethylaceheptylene, which is more enriched in electrons compared with compound (CXI), reacts with acetylenedicarboxylic ester in molar proportions of 1 : 2 to form the 3,5,8,10-tetramethyl derivative (CXXV) (3%), the Diels–Alder adduct (CXXIV) (26%), and the thermally stable diene adduct of cyclohepta[*ef*]heptalene (CXXVI) (12%):



The primary formation of the 1 : 1 adduct (CXXIV) is followed by a secondary cycloaddition with formation of the adduct (CXXV), whose valence isomerisation, accompanied by the opening of the cyclobutene ring, leads to the formation of compound (CXXVI).

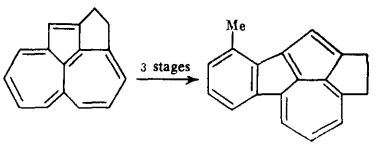
Aceheptylene (CXI) and its derivatives also undergo the cycloaddition reaction (involving very high yields) with ynamines, but the alkyne, which has an enhanced electron density, initially attacks the position most depleted in electrons. The reaction of (CXI) with *N*,*N*-diethyl-1-propynylamine probably proceeds via the formation of the intermediate (CXXVII) and the cyclic adduct (CXXVIII). The reaction involving the expansion of the cyclobutene ring leads to the thermally unstable cyclonon[*cd*]azulene derivative (CXXIX), whose valence isomerisation to compound (CXXX) and subsequent elimination of diethylamine give a 75% yield of 10-methylbenzo[*a*]cyclopent[*cd*]azulene (CXXXI)—a non-benzenoid analogue of fluoranthene, which cannot be obtained by other methods:





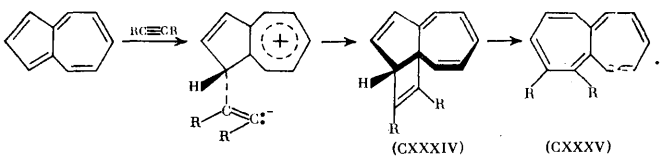
(CXXIX) (CXXX) (CXXXI)

3,5-Dimethyl- and 3,5,8,10-tetramethyl-aceheptylenes react with *N*,*N*-diethyl-1-propynylamine to form 3,5-dimethyl- and 3,5,7,9-tetramethyl-derivatives of the hydrocarbon (CXXXI) in yields of 68 and 92% respectively. A tetracyclic hydrocarbon (CXXXII), for example, can be converted by an analogous procedure into 4,9-dimethyl-1,2-dihydrobenzo-[1,2]dicyclopent[*cd*,*ij*]azulene (CXXXIII) in 21% yield[73]:



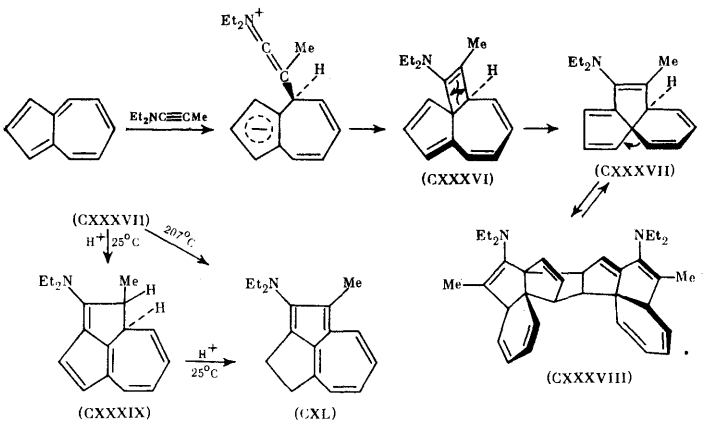
(CXXXII) (CXXXIII)

It is known that azulene can not only undergo substitutional addition reactions with electron-deficient alkynes (for example with dimethyl acetylenedicarboxylate)[75] but also, like electron-enriched alkenes, the thermally induced dipolar cycloaddition via the five-membered ring of the azulene nucleus, the valence isomerisation of the primary adduct (CXXXIV) yielding the heptalene derivative (CXXXV), which is the nearest higher homologue of azulene[53]:



(CXXXIV) (CXXXV)

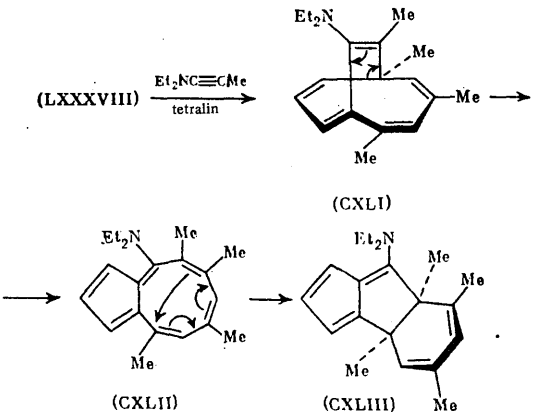
An attempt to make azulene react with *N*,*N*-diethyl-1-propynylamine led to the rapid formation of a 1 : 1 adduct (CXXXVII) in 83% yield[76]. In its crystalline form the bridged spiro-[4,5]decatetraene (CXXXVII) exists in the form of the dimer (CXXXVIII) by virtue of the [4 + 2]cycloaddition of its cyclopentadiene components, while in solution (in benzene and CCl_4 as solvents) the retrodiene synthesis takes place rapidly. Compound (CXXXVII) can be formed via the primary adduct (CXXXVI), which contains the structural element of spiro-[3,4]octa-1,5,7-triene, which readily undergoes[77] 1,5-sigmatropic ring expansion with formation of the dihydropentalene derivative (CXXXIX). The latter is converted into the more stable form (CXL) in 80% yield after 3 h under the conditions of the formation reaction of compound (CXXXIX):



(CXXXVI) (CXXXVII) (CXXXVIII) (CXXXIX) (CXL)

The reaction of azulene with *N*,*N*-diethyl-1-propynylamine in boilbing tetralin gives rise immediately to compound (CXL) in 17% yield, probably also via compound (CXXXVII) as an intermediate stage.

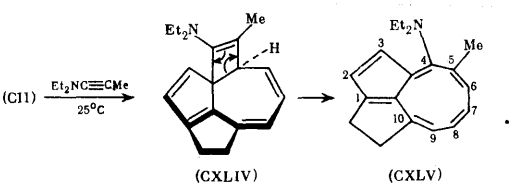
Compound (LXXXVIII) reacts with propynylamine only in boiling tetralin, the cycloaddition being hindered by the alkyl groups in the 4- and 8-positions:



(CXLI) (CXLII) (CXLIII)

The main product proved to be the dihydrocyclopentindene (CXLIII) obtained in 15% yield and containing the resonance-stabilised aminofulvene component. The intermediate state (CXLI), which is incapable of the 1,5-sigmatropic ring expansion owing to the steric hindrance due to the methyl groups but undergoes valence isomerisation to the unstable cyclononatetraene derivative (CXLII), is postulated in this thermally induced reaction. Valence isomerisation is characteristic of cyclononatetraene derivatives[78] and leads to the thermally stable system (CXLIII).

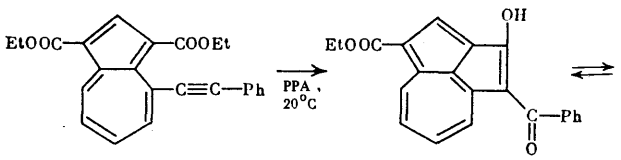
The bridged azulene (CII) reacts with propynylamine even at room temperature with formation of the red-brown crystalline derivative 4-diethynylamino-5-methylcyclopentacyclononatetraene (CXLV) in 47% yield[79]:



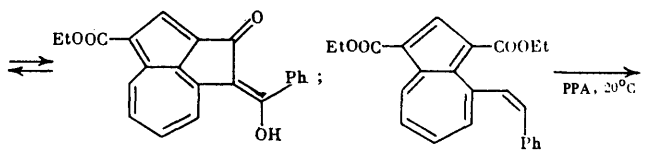
(CXLIV) (CXLV)

The conformation of the nine-membered ring in compound (CXLV) is close to the boat conformation in cyclo-octatetraene.

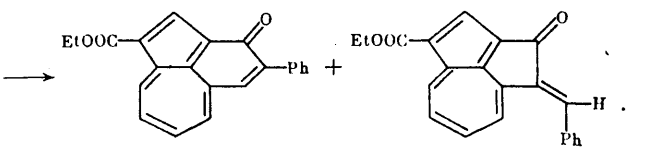
It has been shown recently[80] that diethyl 4-phenylethynylazulene-1,3-dicarboxylate (CXLVI) undergoes intramolecular cyclisation under the conditions of a reaction of the Friedel–Crafts type (treatment with polyphosphoric acid) with formation of the cyclopent[*cd*]azulene derivative (CXLVII).[81] Similarly diethyl-4-styrylazulene-1,3-dicarboxylate (CXLVIII) forms derivatives of benz[*cd*]azulene (CXLIX) and cyclopent-[*cd*]azulene (CL):



(CXLVI) (CXLVII)

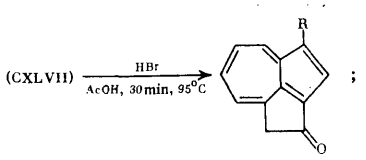


(CXLVIII)



(CXLIX) (CL)

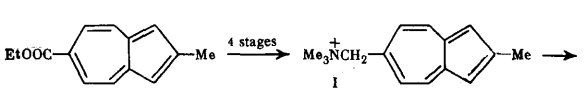
Treatment of compound (CXLVII) with 48% hydrobromic acid in acetic acid leads to the formation of the products of the elimination of the benzoyl and partly the ethoxycarbonyl groups [compounds (CLI, a and b)]:



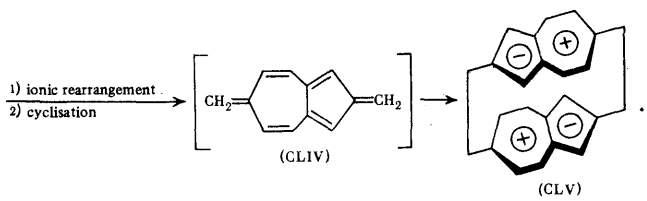
(CLI, a and b)

R = H (a), COOEt (b) .

The multiplicity of the polycyclic azulenoid systems obtained from simple azulenes with functional groups is not exhausted merely by planar conjugated molecules. In 1976 American workers[82] obtained the first azulene-containing macrocyclic system of *anti*-[2.2](2,6)azulenophane (CLV) from 6-ethoxycarbonyl-2-methylazulene synthesised in 8 stages from propiophenone:



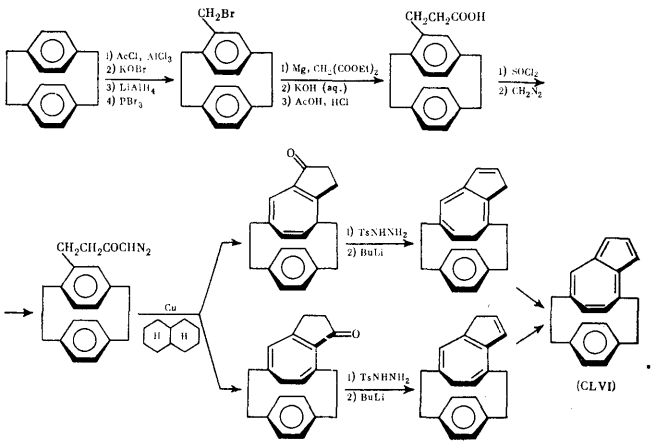
(CLII) (CLIII)



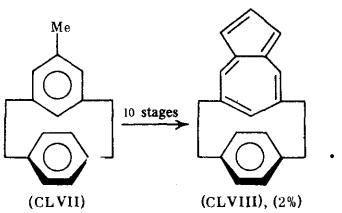
(CLIV) (CLV)

The structure of the cyclophane was demonstrated by electronic spectroscopy and ^{1}H NMR and also mass-spectrometry. Somewhat later, at the end of 1976, Japanese workers published yet another method of synthesis of the azulenocyclophane (CLV), illustrating the extensive possibilities of the intermediate transformations of azulene derivatives[83]. The protonation and electrophilic substitution of the azulenophane (CLV) by tetracyanoethylene have been recently investigated[84].

The syntheses of two types of [2.2]paracycloazulenophanes, (CLVI) and (CLVIII),[85] obtained by an intramolecular reaction involving the insertion of a carbene in [2.2]cyclophanes, have been published:

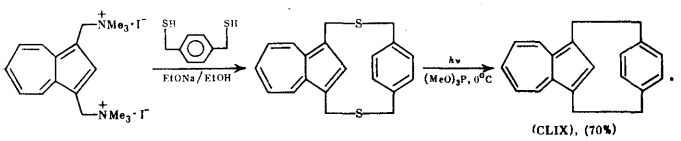


[2.2]Paracyclo(5,7)azulenophane (CLVIII) was obtained from 5-methyl[2.2]metaparacyclophane (CLVII) by a simpler procedure with an overall yield of approximately 2%:



(CLVII) (CLVIII), (2%)

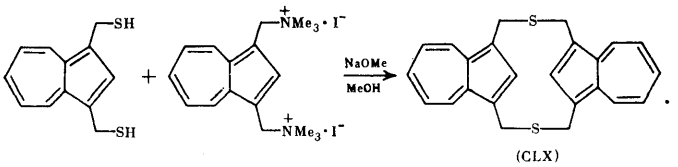
Simultaneously with the compounds indicated above, [2](1,3)azuleno[2]paracyclophane (CLIX) was also obtained[86]:



(CLIX), (70%)

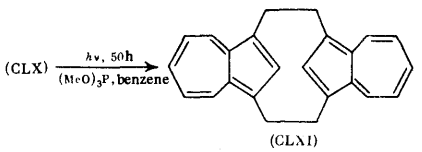
The condensation of 1,3-di(mercaptomethyl)azulene with 1,3-di(methyltrimethylammonia)azulene di-iodide in dry methanol with NaOMe (a high dilution technique is used) gives a

54% yield of 2,13-dithia[3.3]azulenophane (CLX):[87]



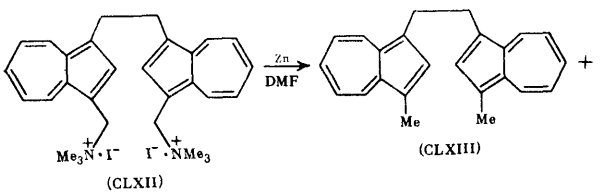
(CLX)

The photodesulphurisation of compound (CLX) in solution in trimethylphosphite–benzene gives rise to [2.2](1,3)-azulenophane (CLXI) in 16% yield:

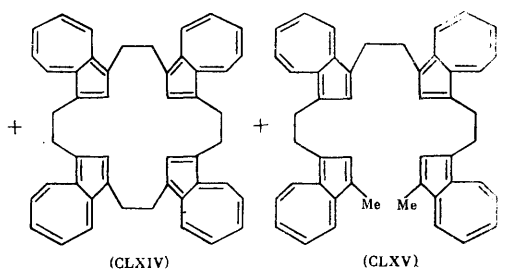


(CLXI)

Treatment of compound (CLXII) with zinc dust in dimethylformamide (DMF) under the conditions of high dilution leads mainly to polymeric products, but 3,3-diazulenyl-1,1-dimethylethane (CLXIII), [2.2.2.2](1,3)azulenophane (CLXIV), and an azulene tetramer with the structure (CLXV) have been isolated chromatographically in yields of 7, 0.1, and 1% respectively[88]:

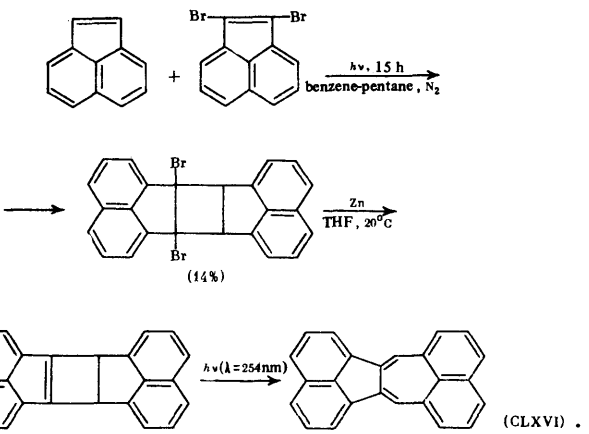


(CLXII) (CLXIII)



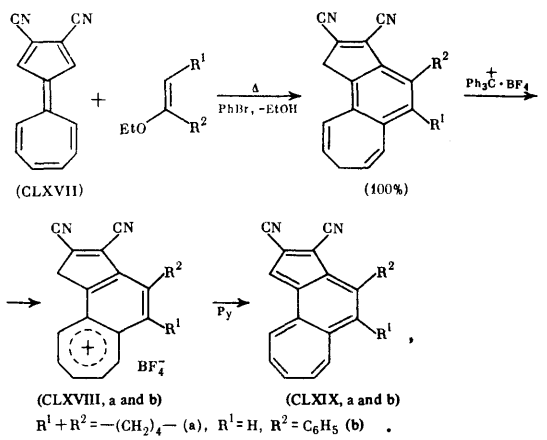
(CLXIV) (CLXV)

The extensive synthetic possibilities of the utilisation of azulene derivatives with functional groups are not exhausted by the carbocyclic systems presented here. Methods of synthesising polycyclic systems with condensed heterocyclic nuclei will be considered below. Before proceeding to these compounds, mention should probably be made of individual representatives of the kind of "non-classical azulenoid systems" obtained recently, in which the role of the seven-membered ring is assumed by another conjugated system, whose structure does not resemble that of the tropylium cation but which is capable of carrying a partial positive charge delocalised over the system. The hydrocarbon (CLXVI), obtained by a combination of photochemical and chemical methods[89], can serve as a representative of such "non-classical systems":



(CLXVI).

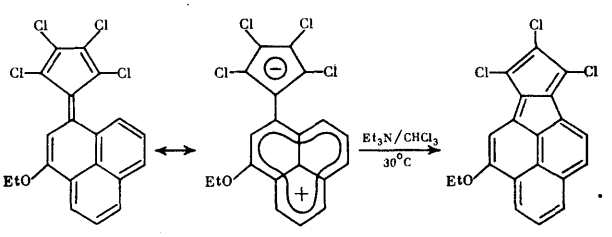
Stable derivatives of phenazulene (CLXIX, a and b), obtained by the [12 + 2] addition of ethoxycyclohexene or α-ethoxystyrene to 8,9-dicyanosesquifulvalene (CLXVII), have an intense blue-violet colour and are very weakly basic, but are protonated by concentrated H_2SO_4 in acetic acid to compounds (CLXVIII, a and b):[90]



(CLXVII) (100%) (CLXVIII, a and b) (CLXIX, a and b)

$R^1 + R^2 = -(CH_2)_4-$ (a), $R^1 = H$, $R^2 = C_6H_5$ (b).

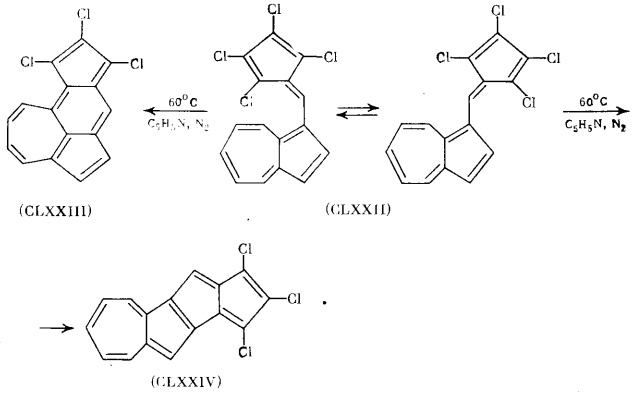
Japanese workers have reported[91,92] that the dehydrochlorination of 9,10,11,12-tetrachloro-2-ethoxypentaphenafulvalene (CLXX) by triethylamine leads to a new pentacyclic conjugated system—6,7,8-trichloro-4-ethoxypentaleno[1,2,3-*cd*]phenalene (CLXXI):



(CLXX) (CLXXI)

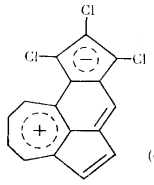
Depending on the nature of the solvent, the ring closure reaction takes place in acetone and n-heptane in 45 min and 10 h respectively. On the basis of these data, the authors proposed an ionic reaction mechanism. If the ionic reaction

does indeed occur, one can assume that a similar intramolecular cyclisation would occur in an alternative form of the molecule, which has a polar electronic structure and is sterically more preferable. The synthesis of the previously unknown tetracyclic conjugated π-electron system of cyclohept[*cd*]-*sym*-indacene (CLXXIII),[93] which can be regarded as an isomer of cyclohepta[*a*]phenalene,[94] was undertaken as an initial test of this hypothesis:



(CLXXIII) (CLXXII) (CLXXIV)

Both NMR data and LCAO-MO calculations for the carbon skeleton of compound (CLXXIII) suggest that the polar structure (CLXXIIIa), similar to that of sesquifulvalene, predominates in the true state of compound (CLXXIII):



(CLXXIIIa)

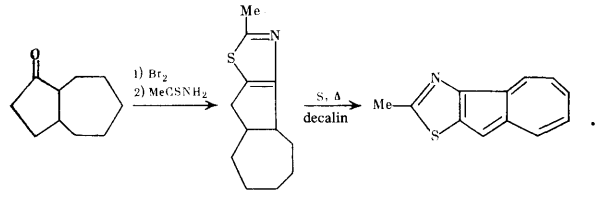
The structure of the alternative product (CLXXIV) has not been finally established although the authors ascribe to it the structure indicated on the basis of mass-spectrometric data and the positions of the absorption bands in the electronic spectrum. Compounds (CLXXIII) and (CLXXIV) are unstable.

The chemistry of such azulene-like polycyclic systems, which sometimes do not obey the Hückel rule, is a matter for the future and is of great theoretical interest from the standpoint of synthesis, stability, and chemical and physicochemical properties.

III. STRUCTURES WITH CONDENSED NITROGEN-, SULPHUR-, AND OXYGEN-CONTAINING HETEROCYCLES

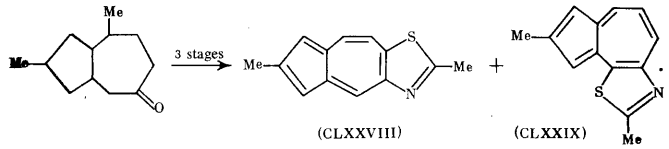
1. Total Syntheses Involving Dehydrogenation

As already mentioned, we include among the total syntheses methods whereby polycyclic azulenes are obtained employing starting materials which are not azulene derivatives and which usually involve a dehydrogenation stage. For example, the bromination of bicyclo[5.3.0]-1-decanone (CLXXV) and subsequent treatment of the resulting α-bromoketone with thioacetamide lead to the thiazole derivative (CLXXVI), which is dehydrogenated by sulphur to 2′-methylthiazole[4′,5′ : 1,2]-azulene (CLXXVII),[95] whose ultraviolet spectrum is close to that of 1,2-benzazulene:



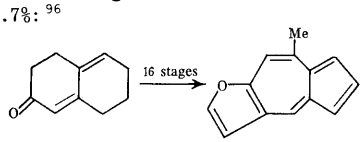
(CLXXV) (CLXXVI) (CLXXVII)

Similarly, 2,8-dimethylbicyclo[5,3,0]-5-decanone gives rise to the two isomeric compounds (CLXXVIII) and (CLXXIX) in proportions of 7 : 1 respectively:



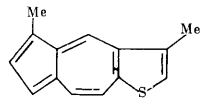
(CLXXVIII) (CLXXIX)

The synthesis of 3,8-dimethylazuleno[6,5-*b*]furan (CLXXX) from naphthalene derivatives has been patented. The synthesis consists of 16 stages and the overall yield of compound (CLXXX) is 0.7%:[96]



(CLXXX)

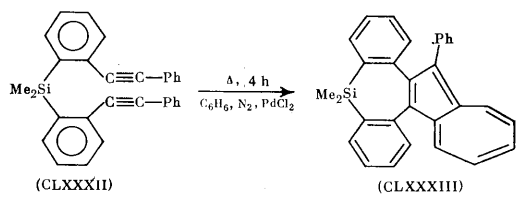
When the sequiterpene fraction of camphor oil is dehydrogenated with sulphur, a small amount of 3,5,8-trimethylazuleno[6,5-*b*]thiophen (CLXXXI) is formed together with *S*-guaiazulene and vetivazulene[97]:



(CLXXXI)

2. Syntheses Based on Acetylenic Derivatives and Other Methods

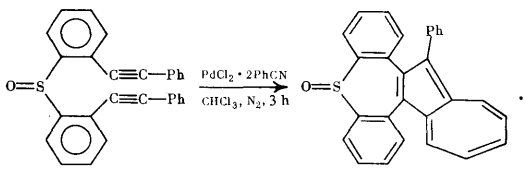
The catalytic rearrangement of the silicon-containing acetylenic hydrocarbons (CLXXXII), leading to a 30% yield of 5,5-dimethyl-10-phenylazuleno[1,2-*d*]dibenzo[*bf*]silepin (CLXXXIII) has been reported[98]:



(CLXXXII) (CLXXXIII)

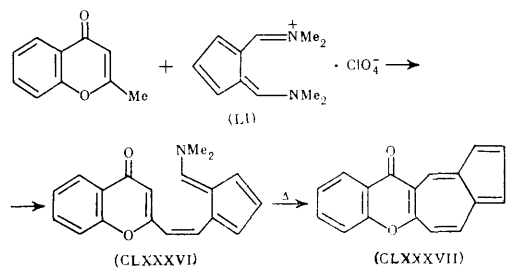
Later the same workers[99] published a synthesis of 5-oxo-10-phenylazuleno[1,2-*d*]dibenzo[*bf*]thiepin (CLXXXV), carried

out by treating the diyne (CLXXXIV) with the complex catalyst $PdCl_2.2PhCN$:



(CLXXXIV) (CLXXXV)

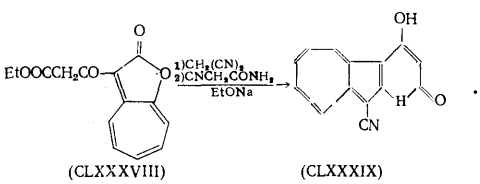
2-Methylchromone has been condensed[50] with a heptamethinium salt (LI) in the presence of sodium methoxide in quinoline, the enamine (CLXXXVI) formed splitting off dimethylamine on heating and giving a 43% yield of azuleno-[6,5-*b*]chromen-12-one (CLXXXVII):



(LI)

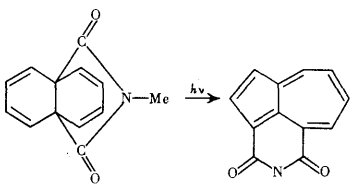
(CLXXXVI) (CLXXXVII)

Japanese workers[100] obtained 10-cyano-4-hydroxyazuleno-[1,2-*e*]-2-pyridone (CLXXXIX) from the 2*H*-cyclohepta[*b*]-2-furanone derivative (CLXXXVIII) by multistage condensation with malononitrile and cyanoacetamide:



(CLXXXVIII) (CLXXXIX)

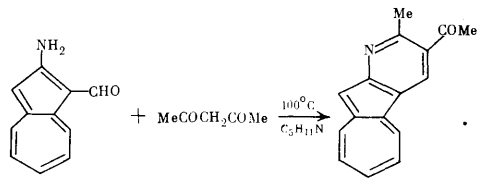
When propellane (CXC) is irradiated with ultraviolet light, the *N*-methylimide of azulene-1,8-dicarboxylic acid (CXCI) is formed in 4% yield together with a series of other compounds[101]. This reaction is of interest because in this case one of the carbocyclic rings contracts with the simultaneous expansion of the neighbouring heterocyclic and cyclohexadiene rings:



(CXC) (CXCI)

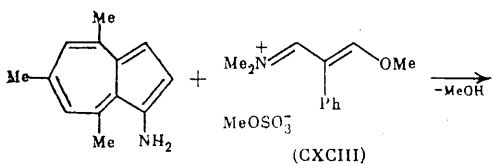
3. Azulene Derivatives in the Synthesis of Heterocyclic Azulenoid Systems

The application of azulenes with functional groups in the synthesis of polycyclic azulenoid systems, including nitrogen- and sulphur-containing heterocycles, constitutes at the present time the most universal method, which has led to the preparation of an extremely large number of a wide variety of compounds of this series. The presence of a free or an acyl-substituted amino-group in the azulene nucleus made it possible to obtain azulenopyridines of various structures as well as other nitrogen-containing derivatives. Thus the condensation of 2-amino-1-formylazulene with acetylacetone in the presence of piperidine makes it possible to obtain 3-acetyl-2-methylazuleno[2,1-*b*]pyridine (CXCII):[102]

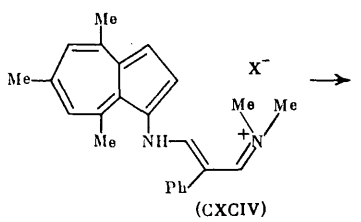


(CXCII)

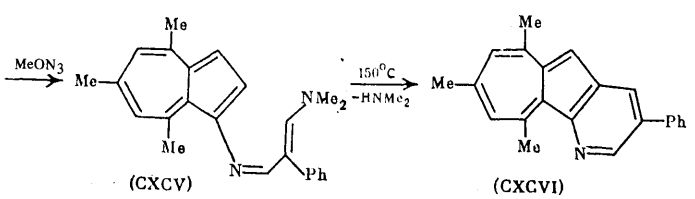
Another isomeric azulenopyridine derivative has been synthesised[57] by the condensation of 1-amino-4,6,8-trimethylazulene with the trimethinium salt (CXCIII). The azulenyltrimethinium salt (CXCIV) is formed initially and is then isolated in the form of the sparingly soluble perchlorate. On reaction with sodium methoxide, the salt splits off perchloric acid and is converted into the amidine (CXCV), which splits off dimethylamine at a temperature as low as 150 °C with formation of 6,8,10-trimethyl-3-phenylazuleno[1,2-*b*]pyridine (CXCVI):



(CXCIII)



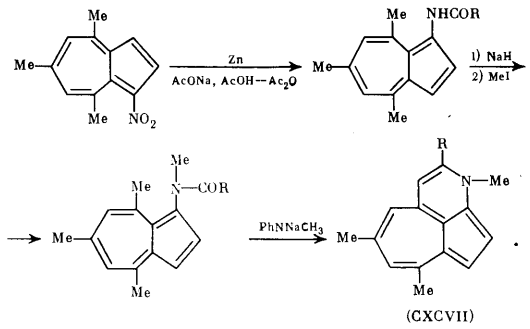
(CXCIV)



(CXCV) (CXCVI)

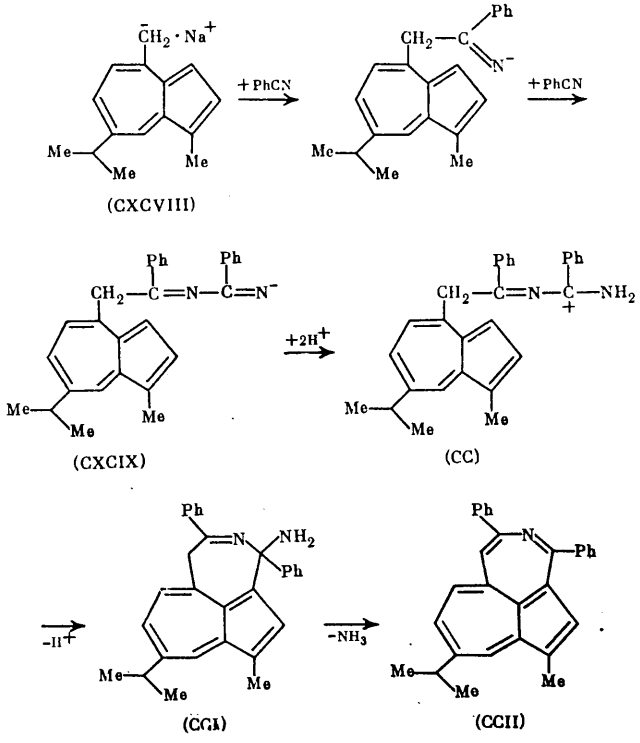
The mobility of the hydrogen atoms of the methyl groups in TMA can be used to synthesise a new pyridine ring condensed along the *cd* faces of the azulene nucleus. An example of this synthesis is provided by the preparation of 1,2,5,7-tetramethyl-1*H*-cyclohepta[*d*,*e*]-1-pyrindine or 1,5,7-trimethyl-2-phenyl-1*H*-cyclohepta[*d*,*e*]-1-pyrindine

(CXCVII) in accordance with the following scheme[103]:

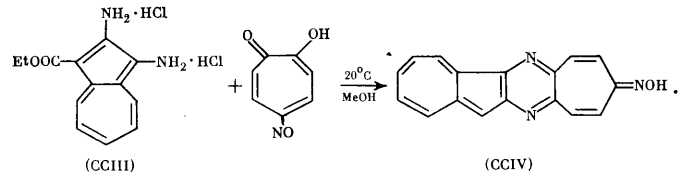


(CXCVII)

The sodio-derivative of guaiazulene (CXCVIII) condenses with benzonitrile to form the amidinium ion (CXCIX) (as the double accretion product), which forms in an acid medium the conjugated carbonium cation (CC), the latter cyclising intramolecularly to the unstable intermediate ketimine (CCI). As a result of the elimination of ammonia from the enamine (the ketimine–enamine tautomerism), the stable aromatic system of 6-isopropyl-8-methyl-2,10-diphenylazuleno[8,9,1-*de*]-azepine (CCII) is formed[104]:

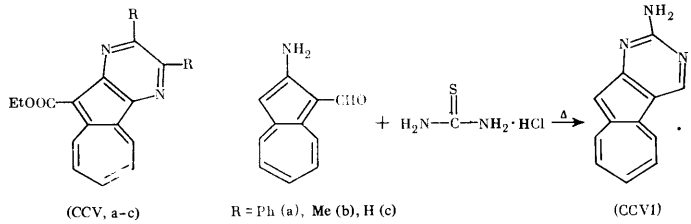


Heterocyclic azulene-containing systems with two nitrogen atoms in the heterocycle can be readily obtained from 1,2-diaminoazulenes. Thus the synthesis of a series of polycyclic derivatives based on 1,2-diamino-3-ethoxycarbonylazulene has been described[105]. When compound (CCIII) was condensed with 5-nitroso-tropolone in methanol, the tetracyclic tropone oxime (CCIV), containing the pyrazine ring in the system, was obtained:



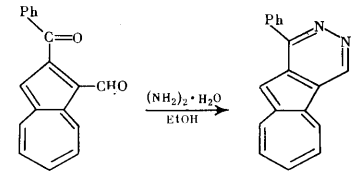
(CCIII) (CCIV)

The condensation of the same diamine with α-dicarbonyl compounds (benzil, diacetyl, or the bisulphite derivative of glyoxal) leads to the corresponding azulenopyrazines (CCV, a–c). The same workers described also the synthesis of the aminoazulenopyrimidine (CCVI):

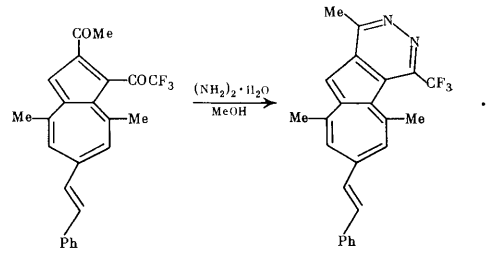


(CCV, a-c) R = Ph (a), Me (b), H (c) (CCVI)

In the presence of two carbonyl groups in the azulene ring, for example the ketone and aldehyde groups, condensation with hydrazine leads to the formation of the azulenopyridazine derivatives (CCVII) [59] and (CCVIII): [39]

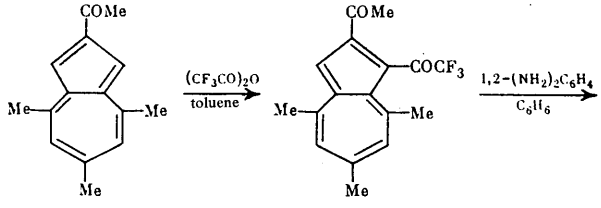


(CCVII)

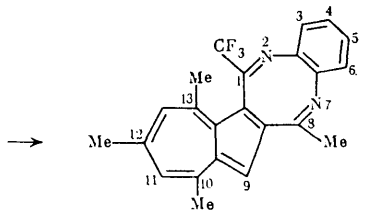


(CCVIII)

Trifluoroacylation of 2-acetyl-TMA (CCIX), obtained by the thermal reaction of TMA with malonic acid[106], results in the formation of the 1,2-diketone (CCX), whose condensation with *o*-phenylenediamine yields the new tetracyclic system 1-trifluoromethyl-8,10,12-14-tetramethylbenzo[*b*]azuleno-[2,1-*f*]-2,7-diazacyclo-octa-2′,4′,6′,8′-tetraene (CCXI): [39]

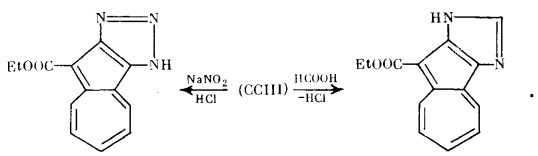


(CCIX) (CCX)



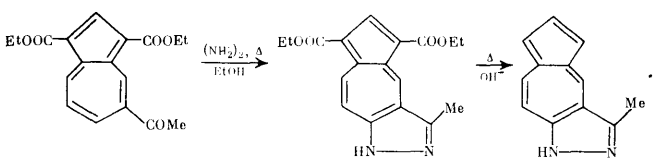
(CCXI)

Derivatives of 1,2-diaminoazulene of type (CCIII) can be readily converted into tricyclic systems containing pyrazole or triazole rings, by their condensation with formic acid or by the diazotisation of one of the amino-groups respectively[105]. The 3-ethoxycarbonyl derivatives of azuleno[1,2-*d*]imidazole (CCXII) and azuleno[1,2-*d*]triazole (CCXIII) have been obtained in this way:



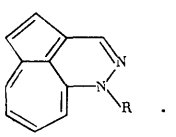
(CCXIII) (CCXII)

The presence of the electron-accepting ketone group in the seven-membered ring, particularly in azulenes in which the electron density is already reduced, such as, for example, 1,3-diethoxycarbonylazulene, the sensitivity of the seven-membered ring to nucleophilic addition increases so much that it permits the synthesis of a pyrazole system, condensed via one of the faces of the seven-membered ring, by the usual condensation of the corresponding derivatives with hydrazine. 5,7-Diethoxycarbonyl-3-methylazuleno[5,6-*d*]pyrazole was obtained in this way[107], the reaction evidently involving the intermediate formation of a hydrazone and its oxidation to the final product. At an elevated temperature the alkaline hydrolysis and decarboxylation of compound (CCXV) lead to 3-methylazuleno[5,6-*d*]pyrazole[108]:



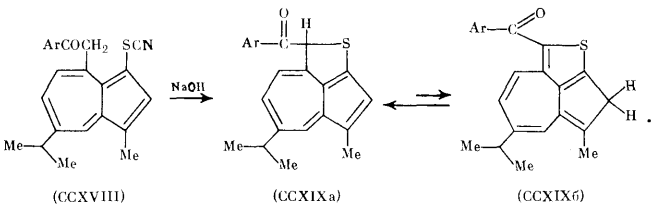
(CCXIV) (CCXV) (CCXVI)

Yet another new polycyclic structure, namely 1*H*-azuleno-[3,10,4-*de*]-1-R-pyridazine (CCXVII) has been obtained[109]:



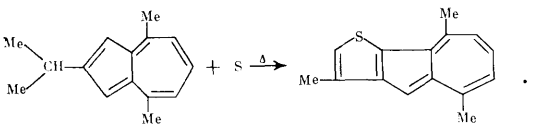
(CCXVII)

Several polycyclic systems incorporating condensed sulphur-containing heterocycles have been obtained from various azulene derivatives with functional groups. Thus the azulenocyclothiophen derivatives (CCXIX) is formed from the thiocyanatoazulenyl ketone (CCXVIII) and it has been established that the azulenodihydrothiophen tautomer (CCXIXa) is thermodynamically more favourable than the heptafulvenothiophen (CCXIXb):[110]



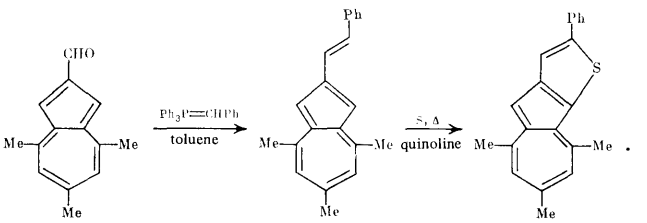
(CCXVIII) (CCXIXa) (CCXIXб)

The high electron density in the 1- (or 3-) position in various alkylazulenes makes it possible to arrive at the azulenothiophen system as a result of the usual dehydrogenation with elemental sulphur. For example, when vetivazulene is heated with sulphur at 200 °C for 4 h in nitrogen, 3,5,9-trimethylazuleno[1,2-*b*]thiophen (CCXX) is formed in 18% yield[111]:



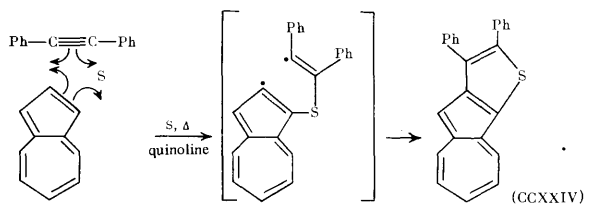
(CCXX)

After it had been established that 1-formyl-TMA undergoes thermal isomerisation to the 2-formyl isomer (CCXXI),[112] a thienoazulene derivative was synthesised via 2-styryl-TMA (CCXXII):[39]



(CCXXI) (CCXXII) (CCXXIII), (22%)

When azulene is heated with sulphur in the presence of diphenylacetylene, dehydrogenation takes place with condensation of the reactants to 2,3-diphenylazuleno[1,2-*b*]-thiophen (CCXXIV) in 8% yield[39]:

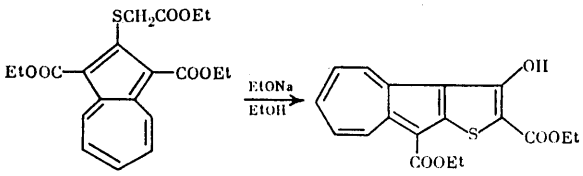


(CCXXIV)

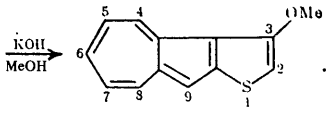
The authors explained the unusual condensation of azulene with diphenylacetylene by the formation of a five-centre intermediate state which is converted into a biradical, the latter recombining to the stable thienoazuleno system. The reaction is accompanied by the formation of a considerable amount of tetraphenylthiophen.

The presence of the thioglycolic residue in the 2-position in azulene made it possible to achieve the cyclisation of the ester (CCXXV) under the conditions of the Dieckmann reaction with its transformation via the hydroxyester (CCXXVI)

into 3-methoxyazuleno[2,1-*b*]thiophen (CCXXVII):[113]

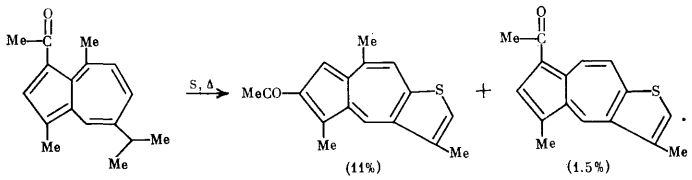


(CCXXV) (CCXXVI)



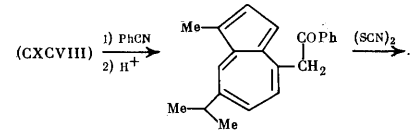
(CCXXVII)

The synthesis of 5- and 7-isopropylazuleno[2,1-*b*]thiophens has been described[114] and the cationic substitution of such systems has been investigated[115]. The thermal reaction of 3-acetylguaiazulene with sulphur, leading to the formation, apart from the 2-acetyl derivative, of azulenothiophens in which the thiophen ring is annellated along the *f* face of azulene [at the C(5) and C(6) atoms] is known[116]:

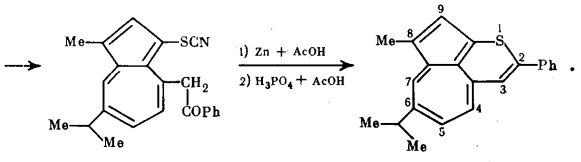


(11%) (1.5%)

The mobility of the hydrogen atoms in the 4-methyl group of guaiazulene makes it possible to obtain the sodio-derivative (CXCVIII), which condenses with benzonitrile to 7-isopropyl-1-methyl-4-phenacylazulene (CCXXVIII). The reaction of the latter with free thiocyanogen, the reduction of the thiocyanate (CCXXIX) with zinc in acetic acid, and intramolecular cyclisation of the intermediate mercapto-derivative, evidently with the enolic form of the phenacyl group, lead to a new azulenoid system—6-isopropyl-8-methyl-2-phenylazuleno[1,9,8-*bc*]thiapyran (CCXXX):[117]



(CCXXVIII)



(CCXXIX) (CCXXX)

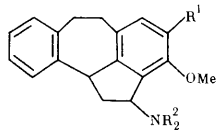
Later a similar system was obtained from TMA.[104] Agreement between the theoretically predicted and experimentally observed mode of electrophilic substitution has been demonstrated for the condensed heterocyclic system (CCXXX).

Thus the Mannich reaction takes place exclusively in the 9-position (yield 79%); the Vilsmeier–Haack formylation of compound (CCXXX) gives rise to the 9-formyl derivative (39%) and the 4-formyl derivative (30%).[118]

The examples of the synthesis of polycyclic azulenes presented above do not exhaust all the possibilities of obtaining more highly condensed and complex carbocyclic and heterocyclic derivatives of this class. The employment of polyfunctional substituted azulenes with polyene residues and heterochain substituents is particularly promising in this field[39].

IV. PHYSIOLOGICAL PROPERTIES OF POLYCYCLIC AZULENES

Until recently, there has been virtually no information in the literature about the physiological activity of polycyclic azulene hydrocarbons and their derivatives, which can probably be accounted for by the fact that many representatives of this class are difficult to synthesise and have been obtained comparatively recently. It is only known that 3-acetyl-2-methylazuleno[2,1-*b*]pyridine as well as 5,7-diethoxycarbonyl-3-methylpyrazolo[4,3-*f*]azulene have been patented as preparations with antipyretic and anti-inflammatory activities[102,108]. 3-Methylpyrazolo[4,3-*f*]azulene has sedative and analgesic properties[108]. Azulene derivatives with analgesic, antidepressant, sedative, and hypotensive properties have been obtained [these derivatives should be more appropriately assigned to the class of hydrogenated azulenylamines of type (CCXXXI)]:[119]



(CCXXXI) R^1 = OH, OMe; R^2 = H, Me .

Certain other derivatives of the series of compounds (CCXXXI) possess similar properties[120]. *l*-3,5β,8β-Trimethyl-4,5,5aα,6,7,8,8aα,9-octahydroazuleno[5,6-*b*]furan[121], which possesses sedative, analgesic, and anticough properties, is known among hydrogenated azulene derivatives. A strong carcinogenic activity is attributed to aceazulenophenalene[49] and a group of other polycyclic azulenes[122]. The azulenofuran (CLXXX) has been patented as a preparation which is effective in the treatment of cancer and stomach ulcers[96].

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Latest Advances and Trends in the Development of Catalysis on Zeolites

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The most important advances in the utilisation of zeolites in catalysis in recent years (1977-1981) and the trends in the development of research in this field are examined.
The bibliography includes 252 references.

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I. INTRODUCTION

Vigorous systematic studies on the utilisation of synthetic zeolites in catalysis have been prosecuted already for more than 20 years. During this period, the efforts of many teams of research workers have laid the scientific foundations for the creation and preparation of zeolitic and zeolite-containing catalysts; factors determining their activity, selectivity, and stability in various reactions have been found, effective ways of regulating the properties of a wide variety of catalysts have been devised, extensive possibilities in the application of zeolitic sytems in catalytic processes have been discovered, considerable advances have been made in the elucidation of the nature of the active centres and the mechanisms of the action of individual systems in reactions of different types, new effective catalysts, including polyfunctional catalysts, have been devised for many petroleum processing and petrochemical reactions, fundamentally new processes based on the utilisation of the characteristic features of the structure of zeolites (selecto-forming, deparaffinisation of oils, etc.) have been proposed, and the industrial manufacture and utilisation of zeolitic catalysts in many chemical processes have been achieved. A consequence of practical importance of the studies which have been carried out is also the formulation of recommendations for the suppresssion of the "parasitic" catalytic activity of zeolitic adsorbents, manifested when they were employed in the drying and purification of olefins and other reactive compounds (formaldehyde, etc.).

The results of studies in this field have been surveyed in a number of monographs, collections, and reviews[1-19]. Vigorous studies are being continued. New possibilities for the application of zeolites in catalysis are being discovered all the time. Specific search for and synthesis on zeolitic materials, necessary for the solution of the most important scientific and technical problems in modern chemistry, are being prosecuted. The research front is extremely broad; more than 250 papers are published annually and numerous patents devoted to various aspects of the synthesis, investigation, and application of zeolitic catalysts are taken out. The volume of information increases very rapidly, which makes it extremely desirable to examine periodically the accumulated data and to analyse the trends in the development of research and advances in the given field of heterogeneous catalysis, which has acquired great theoretical and practical importance. This review is devoted to such analysis of the results of studies published in 1977–1981. The results of earlier investigations are quoted only in so far as it is necessary.

II. EXPANSION OF THE APPLICATIONS OF ZEOLITIC AND ZEOLITE-CONTAINING CATALYSTS

The determination of the efficiency of zeolites as catalysts and components of various catalytic systems in a wide variety of chemical reactions (see, for example, Refs.1, 2, 5, and 8) as well as the discovery of reactions specific solely to crystalline aluminosilicates, such as, for example, the synthesis of ethyl and vinyl derivatives of aromatic compounds by the condensation of $ArCH_3$ with methanol or formaldehyde on the K-, Rb-, and Cs-forms of synthetic faujasites (X and Y zeolites)[20,23] and other reactions[2,5,8], stimulated the search for new applications of these materials in catalysis. The primary results of the research carried out in recent years has been a significant extension of the range of reactions accelerated by zeolitic systems.

1. Organic Reactions

It has been established[24-29] that the *oxidation of lower olefins to carbonyl compounds* can be achieved with a high selectivity on ion-exchange and impregnated zeolitic catalysts containing the Pd^{2+} and Cu^{2+} cations in the presence of water vapour:

$$RCH{=}CH_2 + 0{,}5O_2 \xrightarrow[115-120^{\circ}C]{H_2O} RCOCH_3 .$$

Features of the catalysis such as the necessity for the simultaneous presence in the catalyst of palladium and copper ions (the maximum efficiency is attained for the ratio[24] $Cu^{2+}:Pd^{2+} \cong 6:1$), the deactivation of PdCuNaY on treatment with hydrogen (at 400 °C) and on reduction of M^{2+} to the metal, the

important role of water in ensuring the selectivity and stability of the catalyst, and the decrease of the rate of oxidation of olefins in the sequence ethylene > propene > but-1-ene > *cis*-but-2-ene ≅ *trans*-but-2-ene, which is the same as the analogous sequence in the homogeneous catalytic oxidation of C_nH_{2n} in the presence of $CuCl_2$–$PdCl_2$, etc.[24–29], led to the conclusion that the main stages of the oxidation reaction of olefins, in particular of ethylene to acetaldehyde, on zeolitic systems are similar to those found for solutions of palladium and copper salts[30]. On the basis of the data obtained, zeolitic catalysts for the oxidation of lower olefins to carbonyl compounds can be assigned to the class of heterogenised metal complex catalysts. This conclusion is of fundamental importance and gives rise to a new research field.

The synthesis of ethylene glycol from formaldehyde is catalysed by the zeolites NaX, CaA, and Na-mordenite[31]. The condensation is carried out in the presence of NaOH and proceeds in accordance with the mechanism

$$HCOH + HCOH \rightarrow HOCH_2CHO ;$$
$$HOCH_2CHO + HCOH + NaOH \rightarrow HOCH_2CH_2OH + NaOOCH .$$

This is accompanied by the simultaneous Cannizzaro reaction:

$$HCHO + HCHO + NaOH \rightarrow CH_3OH + NaOOCH .$$

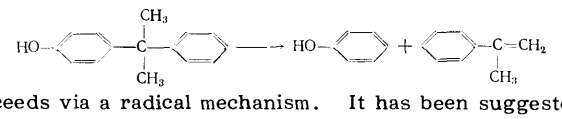
The presence of NaOH in the reaction mixture prevents the formation of free formic acid, which decomposes the catalyst. In the case of Na-mordenite, the degree of conversion of HCOH was ~100% and the selectivity in the formation of glycolaldehyde was ~75% (~24% of HCOH was converted into CH_3OH and HCOOH and <1% was converted into sugars). The synthesis described is of interest as an example of typical base catalysis by zeolitic systems.

Another example of such catalysts is provided by *the crotonic condensation of n-butyraldehyde*, which the authors of the review investigated[32]:

$$C_3H_7CHO + C_2H_5CH_2CHO \rightarrow C_3H_7CH=C(C_2H_5)CHO + H_2O .$$

At atmospheric pressure and 100–200 °C on zeolites X and Y, butyraldehyde is converted with a high (97–100%) selectivity into 2-ethylhexenal and, in contrast to many other reactions (alkylation, disproportionation, oligomerisation, isomerisation, etc.)[33], in this case the M^+-forms of the faujasites are much less active than the specimens containing the M^{2+} and H^+ cations and exhibiting the properties of solid acids (Table 1). Carbon dioxide, which intensifies reactions of the carbonium type accelerated by zeolites[19], has a poisoning effect on the catalysts. These results and the earlier data[34] show that the activity of faujasites in the reaction under discussion is associated with their basic properties.

The efficiency of the NaX zeolite as a catalyst of *the decomposition of p-cumenylphenol with formation of phenol and α-methylstyrene* has been demonstrated[35]. The maximum degree of conversion of the initial substance was observed at 400 °C. It is believed[35] that the reaction



proceeds via a radical mechanism. It has been suggested that the dealkylation of *p*-cumenylphenol be used as a test in the study of catalysts with different types of active centres[35].

Interesting features of the catalytic action of zeolites were discovered in *the halogenation of aromatic compounds*. It has been established[36] that type X zeolites are able to accelerate the chlorination of toluene and halogenobenzenes with formation of *para*- and *ortho*-substituted derivatives whose ratio is significantly higher than for the usual chlorination catalysts, in particular $FeCl_2$. It has been shown[37] that zeolites Y are selective catalysts of the bromination of halogenobenzenes:

$$C_6H_5X + n\ Br_2 \xrightarrow[25-65°C]{CaY} C_6H_{5-n}Br_nX + n HBr$$
(X=F, Cl, Br; n = 1, 2)

Table 1. Dependence of the degree of conversion of n-butyraldehyde into 2-ethylhexenal (%) in the presence of type X and Y zeolites on their composition and the reaction conditions[32].

Zeolite	Without carrier gas	In stream of H_2	In stream of CO_2	Zeolite	Without carrier gas	In stream of H_2	In stream of CO_2
NaX (x=2.5)	45.5	42.2	29.8	0.13 HNaX	24.9	16.8	14.3
0.75 KNaX	53.0	48.2	41.6	0.13 BaNaX	27.8	24.2	19.1
0.65 RbNaX	49.0	46.4	44.6	0.13 NiNaX	34.8	29.5	23.7
0.65 CsNaX	51.6	48.1	46.9	NaY (x=4.4)	23.2	17.4	12.5
0.13 CaNaX	27.5	17.9	13.9	0.70 KNaY	35.8	33.0	28.5
0.81 CaNaX	17.2	13.7	9.1	0.70 RbNaY	35.3	30.4	30.0

Note; $\nu = 1\ h^{-1}$; $C_4H_8O:H_2(CO_2) = 1:0.8$. For the reaction on the MNaX and MNaY zeolites, the temperature is 125° and 200 °C respectively. Here and henceforth the numerals in front of the cations in the formulae of the zeolites indicate the degree of exchange of Na^+ for M^{n+} expressed as a fraction; x is the molar ratio $SiO_2:Al_2O_3$ and ν is the volume flow rate (the ratio of the volumes of the liquid reactant supplied in 1 h to the volume of the catalyst); the molar reactant ratio is always quoted.

Under certain conditions in the preliminary treatment and when catalysts were employed, it was possible to obtain monobromination products enriched in the *para*-isomer. According to Huizinga et al.[38], *the gas-phase chlorination of benzene* (175 °C) on zeolites Y as well as amphoteric aluminosilicate (Al–Si) results in the almost exclusive formation of chlorobenzenes—the products of the substitution of H for Cl, whereas on the ZSM-5 and ZSM-11 catalysts, silicalite, H-mordenite, and SiO_2, mainly hexachlorocyclohexane—the product of the addition of Cl—is formed (Table 2):

$$C_6H_6 + Cl_2 \xrightarrow{ZSM\text{-}5} C_6H_6Cl_6$$
$$C_6H_6 + Cl_2 \xrightarrow{LnY} C_6H_{6-n}Cl_n .$$

The specificity of the catalytic action of high-silica zeolites and SiO_2 was explained by the fact that they promote the preferential homolytic dissociation of chlorine, which leads to the radical addition of Cl, whereas substances containing considerable amounts of aluminium (and acid OH groups) favour an ionic process with formation of electrophilic chlorination products[38].

The efficiency of the MgY, AlY, GaY, and InY zeolites as catalysts of *the condensation of N-2-hydroxypropylethylenediamine with carboxylic acids* has been demonstrated:

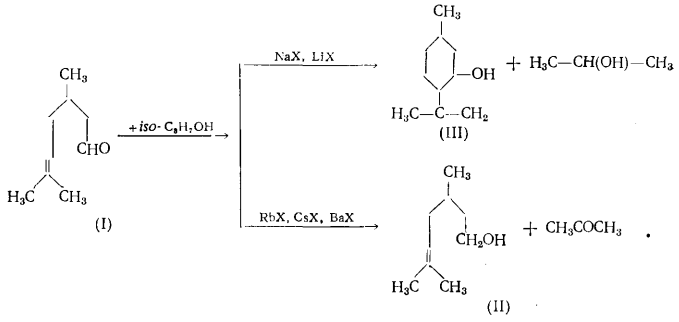
$$RCOOH + H_2NCH_2CH_2NHCH_2CH(OH)CH_3 \xrightarrow[-H_2O]{MNaY} \rightarrow RCONHCH_2CH_2NHCH_2CH(OH)CH_3 \xrightarrow{H_2O} \rightarrow$$
$$\rightarrow \begin{array}{l} H_2C\text{—}CH_2 \\ | \quad\quad | \\ N \quad N\text{—}CH_2CH(OH)CH_3 \\ \diagdown\!\!\diagup \\ C\text{—}R \end{array} ;$$
$$R = C_nH_{2n+1},\ n = 9\text{—}17 .$$

The reaction results in the formation of 2-alkyl-1-hydroxypropylimidazolines and these are used to synthesise surfactants, which have found extensive applications[39]. The $M^{3+}NaY$ zeolites showed the highest activity; when they were employed, the yields of 1-hydroxypropyl-2-nonyl-2-imidazoline were 50–55% (at 160–220 °C). It was established that acid centres with $H_0 = -(3-8.2)$ are active in this reaction.

Table 2. Chlorination of benzene on zeolitic catalysts[38] (175° ± 5 °C, $Cl_2 : C_6H_6 = 5 : 1-10 : 1$).

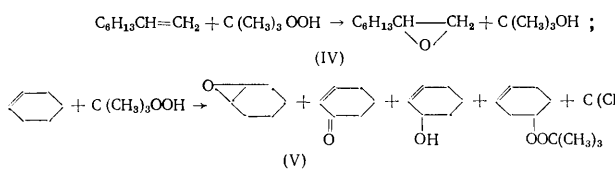
Catalyst	Conversion of C_6H_6, %	Addition products, %	Substitution products, %
NaH-ZSM-5	98	90	10
H-ZSM-5	86	87	13
Ce-ZSM-5	90	81	19
NaH-ZSM-11	86	72	28
Silicalite	97	96	4
H-Mordenite	91	84	16
LnY (SK-500)	100	3	97
Al-Si	94	7	93
SiO_2	82	72	28

The results obtained in the study of the reaction of *citronellal (I) with isopropyl alcohol* led to important conclusions:



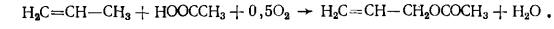
It was shown[40] that, depending on the catalyst, the interaction proceeds via two pathways: with formation of citronellol (II), the product of the reduction of the carbonyl group in compound (I), or of isopulegol (III), the product of the cyclisation of the initial aldehyde. The latter pathway obtains in the presence of the LiX and NaX zeolites, which are relatively coarsely porous and which enable the molecules of compound (I) to assume a configuration favourable for ring closure; the reaction proceeds with a selectivity S close to 100%. The introduction of the large cations Rb^+, Cs^+, and Ba^{2+} ($r > 1.3$ Å) into the faujasite leads to a narrowing of the channels in the aluminosilicate structure and this is believed[40] to force the molecules of compound (I) to assume preferentially a configuration which is relatively little bent; together with other factors, this promotes the selective (S = 85–90%) reduction of compound (I) to the unsaturated alcohol (II). Thus, by altering the dimensions and geometries of the "windows" and cavities in the zeolites as a consequence the steric factors governing the interaction of the reactants, it is possible to control the selectivity of the reactions on the corresponding catalyst.

The epoxidation of olefins by t-butyl hydroperoxide proceeds in accordance with the mechanism



Zeolites X and Y containing transition metal cations (Cu^{2+}, Co^{2+}, etc.) are active in these reactions[41]. At the same time, the initial hydroperoxide decomposes and other side reactions take place. The selectivity depends on many factors and can reach 50% [in the study of Bergk et al.[41] the selectivity S varied in the range 8.9–20.4% with respect to compound (IV) and 6.9–51.2% with respect to compound (V)]. The epoxidation takes place with participation of transition metal ions, evidently via a radical mechanism, which is analogous to the mechanism for the complexes of transition metals and their oxides[41].

Minachev et al.[42] determined the efficiency of zeolitic catalysts in *the oxidative acetoxylation of propene* to allyl acetate—the intermediate in many industrially important organic syntheses:

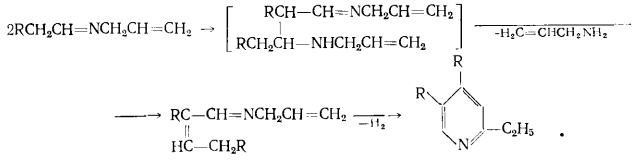


Bimetallic PdCu systems are best for this purpose. Their properties depend on the nature of the exchangeable cation in the zeolite and the type of structure of the aluminosilicate. The dependence of the activity and selectivity of metal-zeolitic catalysts (1% Pd, 0.6% Cu) in the propene acetoxylation reaction on their composition[42] at 1 atm, 180 °C, with a space velocity of the gas mixture of 2333 h^{-1}, and for the ratios $C_3H_6 : CH_3COOH : O_2 = 6 : 1 : 0.5$ is illustrated below:

Zeolite	LiY	NaY	KY	CsY	K, Na-Erionite	Na-Mordenite
Yield, g/litre cat. h	25.6	30.0	35.6	38.4	70.5	28.6
S, %	36.1	39.5	43.2	9.6	92.3	71.2

The catalysts prepared on the basis of K, Na-erionite have the highest activity. The productivity and selectivity parameters obtained with their aid are much better than those corresponding to other catalysts of this process.

In the presence of NiNaY, CoNaY, CrNaY, and FeNaY, *azaolefins undergo heteroaromatisation* with formation of alkylpyridines (yield up to 45–50% of theoretical)[43]:



The reaction proceeds with a high structural selectivity. The behaviour of the catalysts depends not only on their composition and the conditions under which they are employed (temperature and carrier gas—He or NH_3) but also on the initial azaolefin. In the reaction of propylideneallylamine the highest yields of 6-ethyl-3,4-dimethylpyridine were obtained at 350 °C on the 0.05 NiNaY (43% in an He stream) and 0.05 CrNaY (44.2% in NH_3) zeolites. Only 3-ethylpyridine was obtained from ethylideneallylamine on CrNaY. In the aromatisation of cyclohexylideneallylamine the MNaY zeolite showed a lower activity (tetrahydroquinoline was obtained in 8% yield in the presence of 0.05 CrNaY at 350 °C).[43]

Syntheses based on carbon monoxide have undergone further development as a result of the application of zeolitic catalysts. The possibility of converting CO + H_2 into aromatic hydrocarbons[44] and low-molecular-weight olefins[45,46] and CO + H_2O into methane[47,48] has been demonstrated:

$$4CO + 2H_2O \rightarrow CH_4 + 3CO_2 \ .$$

The conversion of methanol (or dimethyl ether) into olefins is of great theoretical and practical value:

$$n\,CH_3OH \rightarrow (CH_2)_n + n\,H_2O \ ;$$
$$n = 2, 3, 4 \ .$$

Various catalytic systems (see, for example, Refs.49–57), including those based on type A and AW-500 zeolites[53], a type X zeolite in the Mn-form[51], dealuminated H-erionite[52], and the ZSM catalyst[49,50,57], are effective in this process. The reaction mechanism apparently depends on the nature of the catalyst. On H-ZSM-5, methanol can be converted with participation of the H^+-acid centres via the mechanism[57]

$$CH_3OH + CH_3OH \xrightarrow{H^+} CH_3OCH_3 + H_2O \ ;$$
$$CH_3OCH_3 + CH_3OCH_3 \xrightarrow{H^+} CH_2{=}CH_2 + 2CH_3OH \ ;$$
$$CH_3OCH_3 + H_2C{=}CH_2 \xrightarrow{H^+} CH_3CH{=}CH_2 + CH_3OH \ ;$$
$$CH_3OH + H_2C{=}CH_2 \xrightarrow{H^+} CH_3CH{=}CH_2 + H_2O \text{ etc.}$$

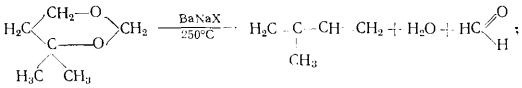
In the case of metal-zeolitic catalysts a reaction pathway involving the dehydrogenation of CH_3OH to formaldehyde, the condensation of the latter, and dehydration of the product is probable[53].

The following reactions in which zeolitic catalysts were shown to be effective are also of theoretical and practical interest:

(1) the synthesis of cyclopropyl methyl ketone from acetylpropyl acetate[58]:

$$CH_3COCH_2CH_2CH_2OCOCH_3 \rightarrow CH_3{-}CO{-}\langle\triangle\rangle + CH_3COOH \ ;$$

(2) the decomposition of 4,4-dimethyl-*m*-dioxan with formation of isoprene[59]:



(3) the addition of α-halogenoethers to asymmetric olefins[60]:

$$C_6H_5CH_2{-}CH{=}CH_2 + ROCH_2Cl \xrightarrow[25°C]{LaNaY} \begin{cases} \rightarrow C_6H_5CH_2CHClCH_2CH_2OR \\ \rightarrow C_6H_5CHClCH(CH_2OR)CH_3 \end{cases} \ ;$$

(4) the synthesis of higher alkanes from methane[61]:

$$n\,CH_4 \rightarrow C_nH_{2n+2} + (n-1)\,H_2 \ ;$$
$$n = 9{-}12 \ .$$

In addition zeolitic catalysts are effective in various oxidative dehydrogenation reactions[62] and in extensive oxidation reactions of organic chloro-compounds (CH_2Cl_2, $CH_2ClCH{=}CH_2$, $CH_2Cl{-}CH_2Cl$, CCl_4), which are important for the elimination of harmful substances from gaseous waste[63]. This, by no means complete list of reactions investigated in the presence of zeolitic systems in recent years, demonstrates very extensive possibilities in the application of zeolites to organic synthesis.

2. Inorganic Reactions

The considerable attention devoted to the study of the properties of zeolitic and zeolite-containing catalysts in inorganic reactions can be accounted for by the relative simplicity of many of the reactions and the convenience of their employment for the elucidation of the nature of the active centres and mechanisms of the action of various systems, the practical value of many of the reactions, in particular, in connection with the problem of the purification of the environment, and also the advances achieved in the industrial application of catalysts based on mordenite in the reduction of nitrogen oxides with ammonia[64,65].

Apart from the reactions involving the isotope exchange of H for D, the oxidation of H_2, CO, NO, NH_3, SO_2, H_2S, and NOCl, the synthesis of NH_3, the decomposition of hydrogen peroxide, ozone, hydrazine, and carbonyl sulphide, the interaction of CO with SO_2 to form COS and CO_2,[2] the ortho–para conversion of hydrogen[66], and the reduction of NO with ammonia[67–70], a number of new processes were discovered in recent years.

The reaction of CO with water vapour:

$$CO + H_2O \rightleftarrows H_2 + CO_2 \ .$$

This reaction is catalysed by the ruthenium complexes $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ with $n < 3$ in zeolites of the type of faujasite, the complexes being formed in the course of the activation of $[Ru(NH_3)_4]^{3+}NaX$ and $[Ru(NH_3)_4]^{3+}NaY$ in the presence of CO at 240–280 °C.[48] Their activity is higher than that of the industrial low-temperature catalyst based on copper.

The reduction of NO with carbon monoxide

$$NO + CO \rightarrow \begin{cases} \rightarrow N_2O + CO_2 \\ \rightarrow N_2 + CO_2 \end{cases}$$

is catalysed by zeolites containing transition metals—Ni, Co, Cu, Cr,[71] Rh,[71,72] and Ru.[73] Depending on the composition of the catalyst, the type of its preliminary treatment, and the conditions under which it is employed, the reaction can proceed with formation of either N_2O and CO_2 or of N_2 and CO_2. According to Minachev et al.,[71] there are at least three temperature ranges in which the characteristics of the reduction of NO are different. At low temperatures (200–300 °C) the product is N_2O and the catalysts are gradually deactivated. Above 350 °C, NO is fully reduced to N_2. It has been observed that the complex $[Rh^I(CO)_2(NO)]^+$, believed to be the reactive intermediate in the reduction of NO to N_2O, is formed from RhY.[72] It has been noted that the composition of the products of the reaction of NO with CO and the influence of temperature are significantly different for rhodium ions in the zeolite and in the case of deposited metallic rhodium[72].

The reduction of NO by molecular hydrogen

$$NO + H_2 \rightarrow N_2 + NH_3 + H_2O$$

is accelerated by the NiY zeolites and the phthalocyanine complexes of nickel in a faujasite matrix (PcNiY), while the CuY, CoY, PcCuY, and PcCoY zeolites are almost inactive[74]. The process selectivity is determined by the reaction temperature and the nature of the ligand environment of the transition metal cations. Only NH_3 is formed on PcNiY, while N_2 is the only product in the presence of the Ni^0/HNaY catalyst obtained by the reduction of NiNaY with hydrogen at 550 °C. In the presence of the NiY zeolite treated with H_2 for 3 h at 350 °C, the degree of conversion of NO at 100 °C was 100%, 62% NO being converted into NH_3 and 38% into N_2.

The synthesis of nitrosyl chloride from nitric oxide and chlorine, i.e.

$$2NO + Cl_2 \xrightarrow{250°C} 2NOCl \ ,$$

has been studied in the presence of catalysts obtained by heating NH_4NaY at 260°, 350°, 450°, and 550 °C.[75] The specimen heated at 550 °C showed the highest activity. A correlation was observed between the rate of reaction and the number of Lewis acid centres in the aluminosilicates.

The decomposition of nitrous oxide

$$2N_2O \rightarrow 2N_2 + O_2$$

is catalysed by type Y and L zeolites and mordenite containing transition metal cations[76–79]. CuNaY and CoNaY are more effective than NiNaY, while the atomic catalytic activity of NiKL is higher than for the NiNa–mordenite and NiNaY systems, in which the degrees of exchange of $Na^+(K^+)$ for Ni^{2+} are similar.

In the reduction of SO_2 with hydrogen sulphide (the Klaus reaction),

$$2H_2S + SO_2 \rightarrow 2H_2O + 3/n\,S_n$$

the activity of the NaX and NaY zeolites is comparable to that of an industrial catalyst (Al_2O_3), while the activity of NaX impregnated with 2% NaOH is higher[80,81]. The reaction is of zero order with respect to SO_2 and of 0.5 order with respect to H_2S. It has been established by infrared spectroscopy that H_2S dissociates heterolytically on the surface of the catalyst ($H_2S \rightleftharpoons HS^- + H^+$), which is consistent with an order of 0.5 with respect to hydrogen sulphide. According to George and Tower[81], the reaction proceeds on basic centres and not on the H^+-acid centres.

New evidence for extensive possibilities in the application of zeolitic catalytic systems to a wide variety of chemical reactions has thus been obtained.

3. Zeolites in Pyrolytic Processes

Pyrolytic processes constitute a promising field of application of zeolite-containing catalysts (ZCC). Thus the maximum yield of ethylene in the thermal decomposition of the propane fraction (40 wt.%) is attained at 850 °C, while in the presence of ZCC such yield is reached at 715 °C, i.e. at a temperature lower by 135 K, the yield of ethylene at 760 °C being 49.5 wt.%.[82] Furthermore, the selectivity of the process in relation to the formation of the desired product increases greatly under the influence of ZCC.

Similar results were obtained in pyrolytic processes involving low-quality petrols in the presence of zeolites and ZCC.[83,84] According to Minachev et al.[83], in the presence of the cationic forms of mordenite it was possible to obtain olefins in higher yields than on the NaA, NaX, and NaY zeolites, chabazite, or K, Na-erionite. The activity of the catalysts and the selectivity of their action depend significantly on the nature of the exchangeable cation M^{n+}. Table 3 shows that the greatest amount of gaseous products and C_2–C_4 alkenes are produced by Ni-mordenite and Co-mordenite. Among the Mn-, H-, and MnH-forms of the zeolite, for which the yields of gaseous products are similar, the decationated specimen has an outstanding selectivity in relation to the formation of olefinic hydrocarbons. These differences can probably be accounted for by the different locations of the Mn^{2+} cations in the Mn- and MnH-mordenites and by the different acid characteristics of the catalysts. The gasification of polyethylene in the presence of the CaX zeolite has also been achieved[85].

These initial studies laid the foundations of the important field involving the utilisation of zeolitic catalysts in pyrolytic processes, whose development is closely related to the synthesis of and research into new thermostable materials.

4. Zeolites as Catalysts and Adsorbents

We believe that a great future awaits the application of zeolites in catalytic processes as adsorbents (or as catalysts and adsorbents). This concerns the utilisation of the molecular sieve properties of zeolites for the selective adsorption of one of the reaction products and the displacement of the equilibrium in chemical reactions. The efficiency of this approach has been demonstrated in relation to the synthesis of esters of carboxylic acids and alcohols with the removal of water by the KA, NaA, and CaA molecular sieves[86–89], the transesterification of esters, $RCOOR^1 + ROH \rightleftharpoons RCOOR^2 + R^1OH$, with selective adsorption of R^1OH,[90–92] and in the synthesis of acetals and ketals[93,94]. The desired products were thus obtained in yields ≥90% (and in many instances in quantitative yields) even in the case of sterically hindered reactants. The adsorbent can be suspended in the reaction mixture or placed in the cartridge of the Soxhlet apparatus[90]. Comparison of the methods for the removal of H_2O or R^1OH. .(CH_3OH) by azeotropic distillation and adsorption on zeolites showed that in the latter case higher yields of products are obtained in a shorter time[7].

Table 3. Pyrolysis of high-quality petrol (O.N. = 42) on cationic forms of mordenite[83] (T = 600 °C, v = 1 h^{-1}).

Cationic form of zeolite	c_1, %	$[C_2-C_4]$, %	α	c_2, %
Li	25.0	57.2	1.44	8.1
Na	78.7	47.5	1.16	5.5
K	49.5	38.2	0.8	5.7
H	55.0	57.3	1.39	7.2
Co	80.0	66.6	3.37	7.0
Ni	81.2	68.8	2.63	6.0
Mn	40.6	51.7	1.29	6.6
MnH	50.4	75.9	3.6	5.7

Notation: c_1 and c_2 are the yields of gas and coke respectively, $[C_2-C_4]$ is the content of olefins in the gas, and α = olefin : paraffin ratio.

The use of zeolites as catalysts and adsorbents simultaneously (either of the same type or of different types and compositions in the two cases) is of special interest. Table 4 presents data[94] obtained for the synthesis of the diethyl acetal of cyclohexanone in the presence of the M^{n+}NaY zeolites as catalysts and the CeNaY and KA zeolites as adsorbents. Evidently, the reaction with KA goes to completion and at the same time the period during which cyclohexanone undergoes a quantitative conversion is shortened; KA is a more effective adsorbent than CeNaY.

5. Industrial Applications of Zeolitic Catalysts

Considerable advances have been made in recent years in industrial catalysis on zeolitic systems. New catalysts have been developed for the cracking[14,95–102], hydrocracking[18,103], and selective hydrocracking ("selecto-forming")[17,18,104–107] of petroleum fractions, the isomerisation of aromatic C_8 hydrocarbons ("octafining")[108,109], and the isomerisation of n-paraffins[110,111], in which zeolite-containing compositions have already been used. The scale of the manufacture and utilisation of catalysts has increased and their assortment

has been expanded. It has become possible to process new types of raw materials.

Catalytic cracking is the process involving the largest-scale consumption of catalysts. At the present time 220000 tonnes of zeolite-containing cracking catalysts are produced annually in the capitalist countries of which 200000 tonnes are employed in fluidised bed apparatus[18]. Catalysts have been devised which diminish the amounts of coke and gas formed and of the sulphur oxides discharged from the regenerator[98,99] and promote the oxidation of carbon monoxide in the smoke gases present in the fluidised bed cracking regenerators—this is achieved by introducing small amounts (<0.001%) of noble metals[95,96]. Compositions have been developed which are effective in the processing of heavy raw materials, are resistant to poisoning by metals, and increase the octane numbers (O.N.) of the fuels obtained[14,18,99]. They are all based on type Y zeolites, which are used in the ultrastable lanthanide (LnY) and magnesium-lanthanide modifications (MgLnY). Polyzeolitic systems incorporating, together with faujasites, also zeolites of other types (ZSM, mordenite, erionite, and ferrierite), which permit a finer control of the composition of the product formed, in particular they make it possible to increase the yields of propene and butenes, have been proposed recently[18]. Further developments in this field will evidently tend to increase the stability of the catalyst in relation to various influences, including the influence of admixtures in the raw material, to improve the selectivity of the catalyst, and to promote the maximum utilisation of these possibilities.

Table 4. Synthesis of cyclohexanone diethyl acetal using zeolitic catalysts and adsorbents[94].

Catalyst	t_a, °C	Adsorbent	$\tau_{50\%}$, min	η, %	τ, min
0.62 CeNaY	200	—	180	52	240
0.62 CeNaY	200	CeNaY*	14	71	60
0.62 CeNaY	200	KA	13	99.9	45
0.61 LaNaY	200	KA	19	99.9	60
LnY	200	KA	34	99.9	120
SK-500 (LnHY)	200	KA	11	99.9	45
0.67 NH_4NaY	340	KA	20	99.9	105
0.68 MgNaY	400	KA	—	3.1	150
0.75 CaNaY	400	KA	90	99.9	250

Note. A mixture of cyclohexanone (0.05 mol) and ethanol (0.2 mol) in n-hexane (75 ml) was stirred with the catalyst (4 g) and powdered KA (10 g) at 0 °C; t_a is the catalyst activation temperature, $\tau_{50\%}$ the time of attainment of 50% conversion of cyclohexanone and η the final conversion of cyclohexanone.

*In this case 14 g of the 0.62 CeNaY zeolite was taken in order to accelerate the reaction and displace the equilibrium.

Hydrocracking is the second process in which zeolitic catalysts are used on a wide scale (the annual consumption exceeded 1000 tonnes; approximately 50% of the starting material subjected to hydrocracking is processed with their aid[18]). They are all based on type Y zeolites and the hydrogenating components are Co, Mo, W, Pt, and Pd. The application of the catalysts is expanding continuously in a varied manner[103,112,113]. Radchenko et al.[103] described in greater detail the existing hydrocracking processes in the USSR and abroad, in which zeolite-containing catalysts are employed, as well as processes developed and designed for industrial use.

The selective hydrocracking (selectoforming) of n-paraffins (mainly C_5–C_9 paraffins) in mixtures with isoparaffins and aromatic hydrocarbons is designed to improve the quality (increase the O.N.) of reforming petrols with simultaneous formation of liquefied petroleum gas (a mixture of propane and butane). A catalyst exhibiting a molecular-sieve activity is used in this process. It is prepared from natural erionite (this is so far the only example of the industrial application of a catalyst made from a natural zeolite)[17,18] or from its synthetic analogue[104,105] and a metal (Ni or Mo). The possibility of employing also catalysts based on a narrow-pore synthetic mordenite has been demonstrated[114,115]. The selective hydrocracking of catalytic reforming petrol, refined petrol, and their mixture on a metal-zeolitic catalyst can yield a basic component with O.N. = 95, which on treatment with ≤15% of isopentane is converted into the non-ethylated petrol AI-93.[106] As a result of the involvement of low-octane refining products in the processing, the consumption of the straight-chain starting material is reduced (by ~20%) in the manufacture of AI-93 petrol[106].

The isomerisation of n-alkanes (the pentane–hexane fractions of petroleum and gaseous and light petrols) yields high-octane components of motor fuels—isoparaffinic hydrocarbons. According to Simoniak et al.[116], the complete isomerisation of normal paraffins in the fraction with a terminal boiling point of 71 °C in combination with catalytic reforming increases the O.N. of petrol by 20 points and yields a product balanced with respect to the O.N. of narrow fractions. A zeolitic isomerisation catalyst (H-mordenite containing a small amount of a noble metal) has been used since 1970 (the high isomer process[117]); at the present time it is already used in tens of different types of apparatus[18]. Various modifications of the Pt–zeolite Y catalysts[111] have also been developed and applied in industry. The Leuna-catalyst 8852 with the composition $Pt/LnCaY/Al_2O_3$ was introduced in 1980.[111]

The isomerisation of aromatic C_8 hydrocarbons (industrial mixtures of xylenes and ethylbenzene) is carried out under hydrogen pressure in the presence of metal-zeolitic systems. The Pt–dealuminated H-mordenite–Al_2O_3 catalyst has a high activity and stability in this process, whose aim is the maximum synthesis of *p*-xylene[108]. The latest catalysts are based on zeolites of type ZSM-5.[17,18,118] Their characteristic feature is a high ratio of their activities in the isomerisation and disproportionation of alkylbenzenes, which amounts to approximately 1000 (for mordenite catalysts, it is close to 70 and for faujasite catalysts it is 10–20).[118] This ensures the formation of *p*-xylene in hitherto unattainable yields and a diminution of the principal side reactions.

The industrial applications of zeolites and zeolite-containing catalysts in many of the other processes described below has begun.

In the alkylation of benzene by ethylene, designed to synthesise ethylbenzene which is converted into styrene and the latter is used in the manufacture of plastics and synthetic rubbers, aluminium chloride has been used as the catalyst hitherto. The problems associated with the application of $AlCl_3$ are generally known. Studies designed to replace $AlCl_3$ by solid catalysts which at the same time meet current requirements including those concerning the protection of the environment and the improvement of health conditions in the relevant industries, have been prosecuted for many

years. Many zeolitic catalysts have also been proposed[1,2,5,8]. However, it was not until 1977 that ethylbenzene was synthesised on an industrial scale in accordance with the technology of the "Badger" company using a catalyst based on the ZSM-5 zeolite developed by the Mobil Oil Corporation[119-121]. This catalyst does not cause corrosion of the equipment, is inert with respect to admixtures in the starting material, and does not require special storage conditions. The process does not involve the formation of harmful atmospheric and aqueous waste.

According to the results presented in Ref.121, the overall productivity of the existing and planned plant reaches 335000–465000 tonnes of ethylbenzene annually.

The catalytic deparaffination of distillates and oils is carried out on bifunctional metal-zeolitic systems and is used to prepare low-setting fuels and basic oils[122-125]. The best catalysts of the deparaffination of petroleum crude are platinum- or palladium-containing dealuminated H-mordenites[124]. They convert effectively only paraffinic hydrocarbons with normal or slightly branched structures, while sulphur and nitrogen compounds in aromatic hydrocarbons are changed little. Here it is important that predominantly the cleavage of alkanes with formation of gaseous products (principally propane, butane, and pentane), and not their isomerisation, takes place on the M^0/H-mordenites.

A process for the catalytic deparaffination of heavy distillates, whose application makes it possible to produce diesel and boiler fuels from heavy gas-oils, has been developed[122, 123]. The process is carried out on a stationary catalyst (based on the ZSM-5 zeolite) at 260–427 °C, a pressure of 21–42 atm, and with circulation of the hydrogen-containing gas. Fractions with setting points ranging from 6.7° to 54.4 °C and containing up to 50 wt.% of n-paraffins can be deparaffinated (by the selective hydrocracking of normal or weakly branched paraffins). The catalyst is resistant to the action of sulphur and nitrogen compounds, whose content in the starting material can reach 3 and 0.1 wt.% respectively. The period between the oxidative regenerations of the catalyst is 0.5–2 years. The yield of product which begins to boil at 165 °C is 54–91 vol.% with respect to the starting material and its setting point is greatly reduced[122]. The completion of the construction at the refinery of the Mobil Oil Corporation in Wilhelmshaven (Federal Republic of Germany) of a plant for the catalytic deparaffination of heavy gas-oil with output of 600000 tonnes per year has been reported[125]. The process is designed for the synthesis of furnace fuel (FF). Petrol and gas in the proportions FF : petrol : gas = 86 : 7 : 7 are formed together with the furnace fuel (400 °C, 40 atm). The application of this process increases the yield of the intermediate distillates from petroleum by ~5%.[125]

The synthesis of propane from butane[126] is based on the reaction $3C_4H_{10} + H_2 \rightarrow 4C_3H_8$. The catalyst (its composition is not reported) is a zeolite with a low content of an alkali metal, which exhibits hydrogenating properties although hydrogenating components are not specially introduced. The process conditions are as follows: temperature at the inlet to the reactor with a stationary catalyst bed 315–450 °C, pressure 12–23 atm, space velocity of liquid C_4H_{10} 1–3 h^{-1}, and the molar ratio $H_2 : C_4H_{10} = (3–6) : 1$. The highest yield of propane is obtained for a conversion of butane of ~90%. The industrial plant yielded 88.8% of propane and 12.8% of fuel gas for a hydrogen consumption of 1.6 wt.%.[126] The process makes it possible to overcome the shortage of propane and to smooth out the seasonal variations in the manufacture of individual hydrocarbons.

The disproportionation of toluene in the manufacture of benzene and xylenes can be achieved in the presence of various catalysts. When a lanthanide zeolite Y is used, the process is carried out in the liquid phase at 260–316 °C, 45 atm, and a weight velocity of the starting material of 1.5 h^{-1}. The degree of conversion of toluene per pass is ~45%, the yield of benzene is 19.7%, and the yield of xylenes is 23%. The life of the catalyst is 1.5 years[127]. The catalyst, based on the ZSM-5 zeolite, is highly selective and makes it possible to obtain disproportionation products enriched in *p*-xylene[17,18,118].

A series of catalysts for *the hydropurification of petroleum fractions*, based on the GO-115, GO-116, and GK-35 zeolites, have been developed[128-130]. Some results of the employment of the GK-35 catalyst on an industrial plant have already been examined[129].

The reduction of nitrogen oxides by ammonia is so far the only inorganic catalytic process in which zeolitic catalysts have found an industrial application. It is designed to make harmless the waste gases from a number of chemical industries (factories producing HNO_3, etc.). The H-forms of mordenite are effective catalysts of the reaction of NO_x with NH_3 to form N_2 and H_2O.[64,65] The Zeolon-200H catalyst is used in the USA and Canada in several types of plant. A new, cheaper, and more active NC-300 catalyst, having the following chemical composition (wt.%) has been developed recently: 72–80 SiO_2, 17–22 Al_2O_3, 1–4 Fe_2O_3, and <1.5 K_2O; its characteristic feature is the possibility of carrying out the process under milder conditions and in the presence of SO_2 as well as large amounts of water[64,65].

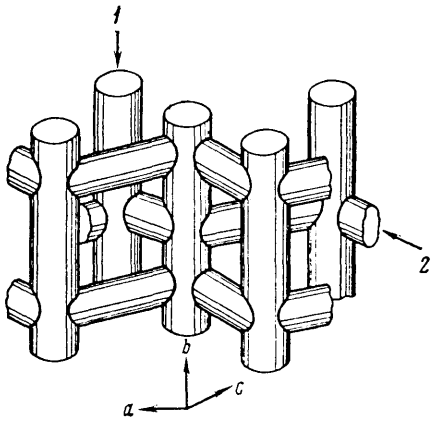
The conversion of methanol into petrol is included by some workers[17,18] among the industrial processes in which zeolitic systems are used. Such synthesis of motor fuel has been proposed by the Mobil Corporation[131-133]. Methanol is converted into a mixture of hydrocarbons having the following typical composition (wt.%): 1.7 C_1–C_2, 6.0 C_3, 16.4 C_4, 19.0 C_5, 16.4 C_6, 13.0 C_7–C_9, and 27.5 C_6–C_9 (aromatic); C_n with $n \geq 11$ are hardly formed, so that the composition (and characteristics) are close to those of petrol obtained from petroleum. This process has attracted attention as the final stage in one of the procedures for the synthesis of motor fuel from solid mineral fuels (or natural gas) in accordance with the scheme coal → synthesis gas ($CO + H_2$) → methanol → petrol. Its development has advanced to the stage involving the sale of licenses and demonstration plant is operating[17,134]. In November 1979 the government of New Zeland decided to manufacture petrol in accordance with the technology of the Mobil Corporation (the output of the plant is 1500 tonnes in 24 h).[17,134] Methanol can be obtained from natural gas. The design of the plant incorporates reactors with a stationary catalyst bed. The construction of a plant for the production of petrol from methanol in a fluidised bed is planned in the Federal Republic of Germany[134]. However, there is as yet no information as to whether the process is being applied on an industrial scale.

Thus the search for new applications of zeolites in catalysis is being prosecuted in several directions.

III. CATALYTIC SYSTEMS BASED ON ZEOLITES OF NEW TYPES

Hitherto approximately 150 structural types of zeolites have been described[135]. The catalytic activity has been studied only for certain types: A, X, Y, L, mordenite, erionite, chabazite, omega, clinoptilolite, offretite[1,2,5,6,8,10,12,15], and

ferrierite[136,137]. In recent years much attention has been devoted to zeolites of the pentasil family[138,139]: ZSM (the Soviet analogues are referred to as TsVK, TsVM, and ultrasil) and silicalite. These zeolites have an unusual structure[138–142], in which the dimensions of the windows and channels are intermediate between those of the windows and cavities in narrow- and wide-pore zeolites (see Figure), which ensures their unusual molecular-sieve properties; the zeolites are characterised by a high thermal stability, resistance to acids, and hydrophobic properties (combined with a low Al content); all these factors are responsible for the unusual nature of their interaction with various substances[141–144]. The SiO_2/Al_2O_3 ratio in the zeolites of the given families varies within wide limits, from approximately 20 to several hundreds and even thousands (specimens with $x = 8660$ have been investigated[144]); silicalite contains virtually no aluminium. Certain characteristics of ZSM-5 and silicalite are compared in Table 5.



Model of the porous structure of the ZSM-5 zeolite and silicalite: 1) linear channel with an elliptical cross-section (5.7 × 5.1 Å) formed by ten oxygen atoms; 2) zig-zag channel with a nearly circular cross-section (5.4 Å in diameter) formed by ten oxygen atoms.

Table 5. Comparison of the properties of the ZSM-5 zeolite and silicalite[46,139].

Property	ZSM-5	Silicalite
Chemical composition	$Na_2O \cdot Al_2O_3 \cdot x\ SiO_2$ ($x = 20 \div 1000$)	SiO_2
Number of Si and Al atoms in unit cell	96	96
Ion-exchange properties	Present	Absent
Crystal structure	Orthorhombic; $a = 20.1$ Å; $b = 19.9$ Å; $c = 13.3$ Å	Orthorhombic; $a = 20.6$ Å; $b = 19.80$ Å; $c = 13.36$ Å
Porous structure	Shown in Figure	Shown in Figure
Sorption of H_2O	Low in the presence of high SiO_2 content	Low
Thermal stability	Increases with increasing silicon content	High

During a short period, the catalytic properties of systems based on pentasils have been investigated in many reactions: in the cracking of hydrocarbons[143–149], in the oligomerisation[150–155] and aromatisation of C_2–C_4 olefins[143,152,153,155–159], in the dehydration of alcohols and other oxygen-containing compounds[160–163], in the conversion of methanol into petrol[17,131–133], olefins[49–57], and aromatic hydrocarbons[143,148,153,156,162,164], in the alkylation of aromatic compounds[145,153,165,166], in the chlorination of benzene[38], in the dehydrogenation of ethanol[161], in the synthesis of a wide variety of compounds from CO and H_2,[45,47,167,168] in the aromatisation of alkanes and cycloalkanes[169,170], in the disproportionation of aromatic hydrocarbons[165,171], in the selective hydrocracking of n-paraffins and methyl-substituted paraffins in mixtures of hydrocarbons of different compositions[122,123], in the isomerisation of n-alkanes[172,173], in the hydrolysis of ethyl acetate[174], and in others[15,138]. Detailed examination of the results is outside the scope of this review. We shall consider certain features of the catalytic action of systems incorporating pentasils.

In contrast to H-mordenite[175], in the presence of the H-form of TsVK n-pentane undergoes mainly hydrocracking and disproportionation with formation of C_1–C_4 alkanes and hexanes and not isomerisation (Table 6). The introduction of palladium into zeolites leads to catalysts in the presence of which isopentane is obtained with high yields and selectivity. Since the concentrations and strengths of the protic acid centres in H-ZSM-5 and H-mordenite are similar[16], the different behaviour of the H-TsVK and H-mordenite catalysts in the conversion of n-pentane can be accounted for by the different distributions of the active centres in the crystal structures of the zeolites and also by the characteristics of their structure.

Table 6. The conversion of n-pentane on catalysts based on TsVK zeolites of different compositions[173] [$p = 30$ atm, $v = 1\ h^{-1}$, $H_2 : n\text{-}C_5H_{12} = 3.2 : 1$ (moles)].

Catalyst	SiO_2/Al_2O_3 (moles)	t, °C	Conversion of $n\text{-}C_5H_{12}$, %	Yield, wt. %		
				iso-C_5H_{12}	C_1–C_4 alkanes	ΣC_6H_{14}
H-TsVK	33.3	250	42.7	9.0	27.0	6.7
H-TsVK	33.3	300	55.0	9.9	41.4	3.7
H-TsVK	83.0	250	37.2	10.0	21.9	6.3
0.5% Pd/H-TsVK	33.3	310	64.8	60.0	3.9	0.9
0.5% Pd/H-TsVK	83,0	330	61,8	59,5	1,4	0,9

Since the dimensions of the windows leading to the channels in the structure of pentasils are greater than in the wide-pore zeolites and smaller than in the narrow-pore zeolites, pentasils manifest a specific molecular sieve selectivity. Thus, according to Rabo[172], the isomerisation of n-hexane on the 0.5% Pt/H-silicalite catalyst yields mainly methylpentanes, while 2,2-dimethylbutane is formed only in insignificant amounts (Table 7). On the other hand, in the presence of the Pt/zeolite Y catalyst the fraction of 2,2-dimethylbutane in isohexanes is approximately 19%. Evidently, the fairly large molecules of 2,2-dimethylbutane (critical diameter $d_{cr} = 6.2$ Å) cannot be desorbed from the channels of silicalite (the latter also does not sorb substances whose molecular dimensions are close to d_{cr} for the neopentane, 2,2-dimethylbutane, and other molecules[172]). We may note that only methane and ethane were obtained from n-hexane in the presence of catalysts based on the H-forms of narrow-pore zeolites[172].

The hydrophobic properties of the ZSM specimens with a high SiO_2 and silicalite content combined with marked organophilic properties makes it possible to employ such catalysts

in reactions carried out in aqueous solutions, as shown in relation to the hydrolysis of ethyl acetate in the presence of H-ZSM-5 ($x = 93.2$).[174] This cannot be done for the majority of other zeolites.

Table 7. Isomerisation of n-hexane on the 0.5% Pt/vapour-stabilised zeolite Y and 0.5% Pt/silicalite catalysts at 15.3 atm and $H_2 : C_6H_{14} = 3:1$ (Rabo[172]).

Catalyst	0.5% Pt/zeolite		0.5% Pt/silicalite		
t, °C	272	262	327	339	351
Conversion of n-C_6H_{14}, %	81.44	77.39	74.74	75.58	76.88
c_1, %	55.42	56.53	68.26	66.22	64.41
c_2, %	18.97	14.84	0.64	2.0	3.67

Note. The silicalite contained 0.6 wt.% of Al_2O_3 as an impurity; it was converted into the H-form with a moderate acidity by ion exchange with NH_4^+ and subsequent heat treatment. The contents of methylpentanes (c_1) and 2,2-dimethylbutanes (c_2) in the C_6 product are quoted.

An important property of pentasils as catalysts and components of catalytic systems is their ability to retain a high activity for a long time (under certain operating conditions), which is significantly higher than for mordenites and other zeolites. Such ability is probably a consequence of the low degree of coke formation when pentasils are employed[16,143,145]. Indeed, using the tracer atom method, it has been established[176] that in the case of mordenite the "yield" of coke is higher by two orders of magnitude than for H-ZSM-5. It has been suggested[16,143,145] that mainly aromatic polyalkylhydrocarbons are a source of coke. They cannot be formed in the limited volume of the channels of pentasils, which limits the "yield" of coke. However, it is noteworthy that the stability of catalysts based on the ZSM, TsVK, and TsVM zeolites depends significantly on their composition and the conditions under which they are employed as well as on the nature of the reactants[143,167]. As a rule, the activity of the catalysts is maintained for a longer period the smaller their residual Na^+ content and the higher the SiO_2/Al_2O_3 ratio; process temperatures greater than or equal to 350 °C are favourable, so that the stability of the pentasil system is apparently determined not only by the rate of formation of coke but also by other factors.

The above examples (see also, the specific nature of the catalytic action of the type ZSM zeolite and silicalite in the chlorination of benzene[38] and a number of studies[46,57,143–145,159,166,167,170] described in Section I) demonstrate the likely usefulness of a comprehensive study of high-silica materials belonging to the pentasil family and others. Among the latest crystalline aluminosilicates, the Fu-1 and Nu-1 zeolites, obtained in systems involving tetramethylammonium compounds[177,178], and TsKF zeolites synthesised in the Na, Rb-, Na, Cs-, K, Rb-, and K, Cs-systems merit attention[179].

IV. CATALYSIS ON POLYZEOLITIC SYSTEMS

A natural development of studies involving different zeolites was the synthesis of polyzeolitic systems and the study of their catalytic properties. Such systems have been investigated in greatest detail in the cracking process[18,101,102]. It has been shown that, in the cleavage of a mixture of hydrocarbons on zeolite-containing compositions incorporating zeolites of the mordenite, erionite, ferrierite or ZSM types together with lanthanide or ultrastable faujasite Y, it is possible to achieve a fine control of the composition of the product formed, in particular the yields of propene and butenes as well as the octane number of the resulting petrol can be increased[18].

By combining the properties of different crystalline aluminosilicates, it is possible to "construct" a wide variety of polyfunctional catalysts of a new type. An example of the latter is provided by the bizeolitic alkylation catalysts which we investigated[180]. They consist of mixtures of zeolites, one of which is active only in the dimerisation of ethylene (NiNaA, NiNaX) and the other is active only in the alkylation of benzene by olefins (for example, CaNaY). In the presence of these catalysts the main product of the interaction of C_6H_6 with C_2H_4 is s-butylbenzene and both single- and two-bed systems are active. Their properties can be regulated by altering the contents of the individual components in the mixture[180]. The polyzeolitic compositions can include the crystallites of both a single type and different types. This application of zeolites in catalysis is very promising and merits further consideration.

V. POLYFUNCTIONAL CATALYSIS ON ZEOLITIC SYSTEMS

Catalysts with polyfunctional activity, which accelerate simultaneously several reactions coupled in a single process, make it possible to carry out in a single stage complex syntheses, including those which are difficult or impossible to achieve with the aid of monofunctional systems[181,182]. Their theoretical and practical importance is enormous. Special attention was devoted to this problem already in the first studies of Rabo and coworkers[183,184] and Minachev and coworkers[1,185,186], carried out during the initial period of the development of catalysis in the presence of synthetic zeolites. Subsequently new catalysts were devised for the hydrocracking and hydroisomerisation of hydrocarbons[6], the hydroalkylation of benzene to phenylcyclohexane[187], the isomerisation of ethylbenzene to xylenes[6,108,109], the hydrocondensation of carbonyl compounds[6,34], the single-stage synthesis of cyclohexane from toluene and H_2,[188] s-butylbenzene from C_6H_6 and C_2H_4 (see our earlier review[189]), and others[6,8].

The effective catalysts for hydropurification processes[128,129], the synthesis of aliphatic hydrocarbons from CO and H_2,[190–193], of olefins from CO and H_2 [45,46] or methanol[53–57], and of aromatic hydrocarbons from C_1–C_5 alkanes[168,194,195] and also from CO and H_2,[44] the disproportionation of paraffinic hydrocarbons[196], and other syntheses[168] were developed in recent years.

In the course of this research, a series of important data were obtained concerning the characteristics of zeolites of different types as components of polyfunctional catalysts, the formation of a wide variety of catalysts, the mechanism of their action, and the method and possibilities of the regulation of their activity, selectivity, and stability, etc. It has been shown[193], in particular, that the use of zeolite-containing systems makes it possible to obtain from CO and H_2 products containing larger amounts of high-molecular-weight hydrocarbons (ceresin) than those obtained on the industrial CO–MgO–ZrO_2–kieselguhr catalyst. On the other hand, it has been observed[192] that the structure of the zeolite can limit the growth of the hydrocarbon chain length. Thus mainly C_1–C_9 hydrocarbons have been obtained on the Ru/NaY ion-exchange catalyst reduced at 300 °C, while in

the presence of Ru/SiO_2 a mixture of C_nH_m, in which paraffins and $\geq C_{12}$ olefins predominated (60%), was obtained under the same conditions of the synthesis [250 °C, molar ratio $CO:H_2 = 3:2$, contact time (with respect to CO) 0.4 s].

The range of catalytic systems with polyfunctional activity has been expanded. It has been established that not only compositions of the metal/zeolite type in the form with H^+ acidity (the commonest catalyst[6]) can exhibit polyfunctional properties. In the alkylation of benzene and its homologues with ethylene, NiY faujasites and $NiO-H^+$–zeolite systems behave as bifunctional catalysts (the interaction of RC_6H_5 with C_2H_4 in their presence proceeds mainly with formation of the s-butylderivatives $RC_6H_4-C_4H_9$ [189]). Alkaline cationic modifications of zeolites X and Y containing Group VIII metals exhibit only a single function in the reactions of hydrocarbons, determined by the metal, catalysing the hydrogenation, dehydrogenation, or oxidation of C_nH_m.[6] On the other hand, they behave as bifunctional systems in the reaction of butyraldehyde with H_2, accelerating simultaneously the crotonic condensation and the hydrogenation of carbonyl compounds coupled in a single process (Table 8); here 2-ethylhexanal and iso-octyl alcohol are obtained in a single stage[32].

Table 8. Hydrocondensation of n-butyraldehyde on metal-zeolitic catalysts[32] (150 °C, $\nu = 1\ h^{-1}$, $C_4H_8O:H_2 = 1:1.5$).

Catalyst	Conversion of n-butyraldehyde, %				
	into butanol	into 2-ethyl-hexenal	into 2-ethyl-hexanal	into 2-ethyl-hexanol	Overall
0.5% Pt/NaX	16.8	10.8	13.0	6.1	51.0
0.5% Rh/NaX	8.4	4.9	29.2	2.8	46.0
0.5% Pd/NaX	1.6	1.6	58.8	1.9	67.0
1.0% Pd/KNaX	1.4	1.0	61.6	1.5	69.5
0.2% Pd/0.65 RbNaX	1.5	4.8	58.0	0.5	65.0
2.0% Ni/HNaX	21.8	1.1	16.1	7.3	47.0
2.0% Co/HNaX	21.5	22.2	20.5	2.7	72.0

Note. The content of the Group VIII metal is expressed in wt.%.

In the presence of Pd/CaY, it is possible to synthesise from C_6H_6 and H_2 either cyclohexane, by altering the temperature (to 200 °C), i.e. by merely hydrogenating benzene, or methylcyclopentane and cyclohexane (at 260–320 °C), i.e. benzene is made to undergo hydroisomerisation and as well as hydrogenation[186]. Thus a catalyst having the same composition can behave as monofunctional and polyfunctional depending on the nature of the reactant and the conditions under which it is employed. This leads to new research fields.

It is becoming increasingly obvious that the possibilities in the application of zeolites in catalytic polyfunctional systems have been by no means fully elucidated. The studies and developments in this field will undoubtedly continue.

VI. ZEOLITIC METAL COMPLEX CATALYSTS

Yet another promising application of zeolitic materials in catalysis has been established—as a matrix for transition metal complexes (TMC) and components of hydrogenised metal complex catalysts. Such systems can be obtained by introducing the prepared complexes into crystallites having the appropriate composition or by synthesising the required compounds within the zeolite cavities (here it is necessary to distinguish cationic complexes and complexes of zerovalent metals[197–199]). The method involving the interaction of dehydrated zeolites containing transition metal cations with the corresponding compounds in the gas phase or solution is most common. It is used, in particular, in the synthesis of phthalocyanine[200], ethylenediamine[201,202], nitrosyl[197–199,203], carbonyl[204–207] and trimethylphosphine[208] transition metal complexes in zeolites X and Y. Catalysts of the TMC–zeolite type can also arise in the interaction of crystalline aluminosilicates with the components of the reaction mixture, as shown for the rhodium-[209–211] and iridium-zeolitic[16,212] catalysts for the carbonylation of methanol with carbon monoxide. The matrices are usually zeolites X and Y, which have the widest pores, ensuring the accommodation of the complex within the structural cavities and the possibility of the coordination of the reactant molecules.

Some characteristics of TMC and zeolites have already been considered[197–199,213]. Important results have been obtained[214–217]; it has been shown with the aid of X-ray photoelectron spectroscopy that the phthalocyanine complexes of nickel and cobalt in faujasite Y are formed mainly in the large cavities of the lattice, being uniformly distributed throughout the volume of the aluminosilicate crystals[214]. With increase of the degree of exchange of Na^+ for M^{2+}, the degree of binding of the cations to the phthalocyanine increases and reaches ~80% for 0.6 MNaY. The photoelectron spectra led to the conclusion that the zeolite behaves not only as a matrix but also as a ligand for complex formation, causing a charge redistribution over the nitrogen and meso-atoms in the phthalocyanine molecule[214,216].

The catalytic properties of TMC–zeolite systems have already been investigated in a fairly wide range of reactions, some of which are listed in Table 9. A number of characteristic features of the catalytic action of these systems have been discovered. According to Gusenkov et al.[225], in the presence of CuY the decomposition of epoxycyclohexane takes place non-selectively with vigorous coke formation. On the other hand, in the presence of copper-phthalocyanine in the zeolite, $C_6H_{10}O$ undergoes dehydration with formation of cyclohexadiene (100% selectivity). In the presence of the ethylenediamine complex of copper in faujasite, only benzene is obtained, i.e. the mode of reaction is determined by the nature of the ligand environment of the transition metal in the TMC in the zeolite[225]. Another example of an appreciable influence of the formation of complexes by M^{n+} in crystalline aluminosilicates on the selectivity of the corresponding catalysts may be provided by the dimerisation of propene in the presence of phosphine complexes of Ni^{2+} in zeolites X, namely $[R_3P.Ni]X$.[40] Depending on R, the main reaction products obtained are methylpentenes or 2,3-dimethylbutenes (when R is large; see Table 2); this is the result of the steric influence of the ligand PR_3, which determines the type of orientation of the π-bonded propene molecule in the olefin dimerisation stage. Thus new interesting possibilities have arisen for the regulation of the activity and selectivity of catalysts.

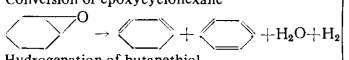
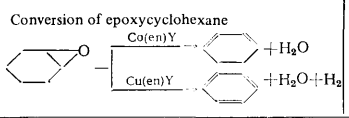
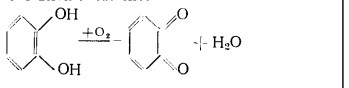
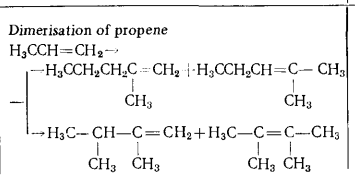
VII. MODIFICATION OF ZEOLITIC CATALYSTS

In view of the polyfunctionality and "universality" of the catalytic action of zeolites, there exists the acute problem of the controlled alteration of the selectivity of zeolitic catalytic systems and in particular of increasing their stability.

There are several ways in which the catalytic properties of zeolites can be regulated. The simplest and most frequently employed method involves varying the composition and conditions of the preliminary treatment of the catalyst[19].

The composition can be altered in the course of the synthesis of the zeolite by substituting the exchangeable cations, by extracting some of the aluminium atoms (dealumination) or silicon atoms from the skeleton, and by other procedures.

Table 9. Catalytic reactions in the presence of TMC–zeolite systems.

Complex, zeolite	Reaction	References
$[Cu(NH_3)_4]^{2+}$ $[Co(NH_3)_2]^{3+}$ in type Y zeolite	$NH_3+O_2\rightarrow N_2+H_2O$ $NO+NH_3\rightarrow N_2+N_2O+H_2O$	[217] [218]
Rhodium carbonyl complexes in type Y zeolite	Hydroformylation of olefins $RCH=CH_2 + CO + H_2\rightarrow RCH_2CH_2CHO + RCHCHO$ (CH$_3$)	[206]
Phthalocyanine complexes of Ni, Co, Fe, and Cu in type Y zeolites	Dehydrogenation of cyclohexane Dehydrogenation of isopropyl alcohol $NO+H_2\rightarrow N_2+NH_3+H_2O$ $CO+O_2\rightarrow CO_2$ Oxidation of cysteine Conversion of epoxycyclohexane  Hydrogenation of butanethiol $C_4H_9SH+H_2\rightarrow C_4H_{10}+H_2S$	[219–222] [220–222] [74] [223] [224] [225] [226]
Ethylenediamine complexes of Co^{2+}, Mn^{2+}, Cu^{2+}, and Ni^{2+} in type Y zeolites	Conversion of epoxycyclohexane 	[225]
	Oxidation of catechol 	[201]
$[Co^{3+}(NH_3)_nNO]^{2+}Y$, $[Co(en)_2]^{3+}Y$, $[Co(trien)]^{3+}Y$*	$NO+NH_3\rightarrow N_2+N_2O+H_2O$	[227]
$[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ in type X and Y zeolites	$CO+H_2O\rightarrow CO_2+H_2$	[47]
Phosphine complexes of Ni^{2+} in type X zeolites: $[R_3P.Ni]X$	Dimerisation of propene 	[40]

Notation: en = ethylenediamine and trien = triethylenetetramine.

In the studies, carried out in recent years, many of these methods were developed further. In particular new methods were proposed for the dealumination of aluminosilicate zeolites, which make it possible to obtain high-silica materials with high chemical and thermal stability. One of these is based on the repeated ion exchange of the initial aluminosilicate with NH_4^+ ions and the hydrothermal treatment of the product in combination with the extraction of non-skeletal aluminium by inorganic acids (HCl or HNO_3).[228,229] Specimens of type Y zeolite in the ratio $SiO_2/Al_2O_3 \geq 100$, which retain their structure even after heat treatment at 1150 °C for several hours, were prepared by this method[228].

The method of dealumination with the aid of $SiCl_4$ is of great interest[230]. It is based on the reaction

$$M_{1/n}[AlO_2(SiO_2)_x] + SiCl_4 \rightarrow 1/n\ MCl_n + AlCl_3 + [(SiO_2)_{x+1}],$$

where M is a cation with a charge n. The process consists of a single stage and is carried out in the absence of water vapour. The zeolite (NaY, NH_4Y, etc.) is dehydrated in a vertical tubular reactor at ~380 °C in a stream of dry nitrogen, after which nitrogen saturated at room temperature with $SiCl_4$ is passed through it, while raising the temperature in the reactor to the specified value (460–560 °C) at a rate of 4 K min^{-1}. The treatment is continued for several hours (≥2 h). The aluminium is removed partly in the form of $AlCl_3$ and is partly converted into the complex $M[AlCl_4]$ {$Na[AlCl_4]$ in the case of NaY}, which is washed off with water. The degree of dealumination depends mainly on the reaction time τ and to a lesser extent on the final temperature of the treatment. In the case of NaY (x = 5.04) for τ = 2 h and 500–560 °C, products with x ranging from 40 to 100 and distinguished by a high crystallinity were obtained[230].

When $SiCl_4$ is used as the dealuminating agent, direct substitution of Al in the faujasite skeleton for Si is believed[230] to occur. The above method is inapplicable to narrow-pore zeolites, since $SiCl_4$ cannot penetrate into the cavities of the crystal structure[230].

Variation of the chemical composition, the method of preparation, and the type of preliminary treatment are only some of the procedures for the specific alteration of the activity, selectivity, and stability of zeolitic catalysts. "Secondary" modification methods are also used: the addition of various substances to the reaction zone (see the review of Minachev and Isakov[19]), complex formation with the exchangeable metal cations, and others (see below) which have more specific applications. The promoting effect of NO_2, SO_2, CO_2, HCl, H_2S, and Cl_2 on CaY in the catalysis of the dehydration of isopropyl alcohol[231], of SO_2 on the MNaX and MNaY zeolites in the isomerisation of butenes[232–236], and of H_2S on MNaY in the cracking of cumene, the disproportionation of toluene, the cracking and disproportionation of xylene, and the dehydration of isopropyl alcohol[237] has been established. The conclusion[19,238] that the application of systems in the presence of other substances permits not only the intensification of catalytic processes and a change in their selectivity but also a more complete determination and ultilisation of the possibilities of zeolites as catalysts has been confirmed. Valuable information about the nature of their activity and the mechanism of their action is obtained at the same time.

A procedure has been developed for the modification of catalysts comprising the ZSM and TsVK zeolites by phosphorus[17,165,166,171], boron[166,171], magnesium[165,171], antimony[239], and vanadium[159] compounds, whereby it has been possible to increase sharply the selectivity of the processes involving the disproportionation of toluene[17,165,171,239], the aromatisation of C_2–C_4 olefins[159], and the alkylation of toluene by methanol[166,239] to form p-xylene. Table 10 presents data obtained in the conversion of C_2–C_4 olefins. Evidently, in the presence of the TsVK zeolite without vanadium, the main component of the alkylbenzenes C_8H_{10} is m-xylene. The introduction of 5 wt.% V_2O_5 into the zeolite lowers the overall degree of conversion of C_nH_{2n} and the yields of the liquid catalytic reaction products and aromatic hydrocarbons (most pronounced in the case of C_2H_4) with a simultaneous marked increase of the fraction of p-xylene in the mixture of the alkylbenzenes C_8H_{10}. The p-isomer of ethyltoluene also predominated among the aromatic hydrocarbons C_9H_{12}.[159]

The causes of the observed effects have not yet been finally elucidated. It has been suggested[159,165,166] that they are associated with the partial blocking of the channels in

pentasils by the modifying compounds, which entails a decrease in the rate of diffusion of the molecules of *m*- and o-xylenes (in the general case *m*- and o-dialkylbenzenes) from the cavities in the crystal structure to the gas phase. However, the steric hindrance arising under these conditions is apparently not the only factor, particularly since the distribution in the catalysts of modifying agents of various types but inducing similar changes is unknown. According to Hughes[118], the modification of H-ZSM-5 with phosphorus (derived from phosphite) diminishes the strength of the acid centres, which explains the decrease of the activity of the catalyst usually observed[166,171] (see also Table 10), and can make a significant contribution also to their selectivity, for example, by altering the isomerising capacity of the catalysts. It is important to emphasise that the method of modifying the ZSM and TsVK zeolites described leads to the possibility of developing new stereospecific catalytic processes for the synthesis of *para*-substituted aromatic compounds.

Table 10. The influence of the composition of the catalyst on the aromatisation of C_2–C_4 olefins[159] [500 °C, v = 500 h^{-1}, $SiO_2 : Al_2O_3$ (in zeolite) = 70.5 : 1].

Initial olefin	η, %	W, %	c, %	Aromatic hydrocarbons, %				Composition of C_8 alkylbenzenes, %			
				C_6H_6	C_7	C_8	C_9–C_{10}	*p*-xylene	*m*-xylene	*o*-xylene	ethylbenzene
Catalyst-initial TsVK (0.7% Na_2O)											
C_2H_4	84.0	44.7	97.3	12.4	57.8	27.8	2.0	12.5	65.2	13.7	8.6
C_3H_6	86.3	40.0	79.7	7.9	33.5	46.3	12.3	22.0	50.4	19.0	8.6
n-C_4H_8	89.9	52.5	87.3	8.0	51.6	39.3	1.1	16.3	69.3	9.7	4.7
iso-C_4H_8	97.0	43.8	71.9	8.3	28.6	46.4	16.8	21.6	48.9	18.6	10.9
Catalyst-TsVk + 5% V_2O_5											
C_2H_4	23.7	7.1	91.1	5.8	34.5	48.9	10.8	78.7	6.4	0.1	14.8
C_3H_6	68.3	24.8	60.3	4.2	40.0	37.8	18.0	75.4	9.1	3.3	12.2
n-C_4H_8	73.4	35.9	75.3	4.0	30.8	54.2	11.0	82.8	10.0	1.1	6.1
iso-C_4H_8	78.4	39.9	71.2	4.4	35.4	50.4	9.8	79.1	8.6	1.1	11.2

Notation: η = conversion of C_nH_{2n}, W = yield of liquid catalytic reaction products, and c = content of aromatic hydrocarbons in catalytic reaction products.

*The contents of benzene and C_7–C_{10} alkylbenzenes are quoted.

In many instances the method involving controlled partial saturation of catalysts with coke has been effective[166,240]. It has been found that this procedure permits a significant increase of the selectivity and stability of catalysts and an increase in their useful life before regeneration. It has been shown, in particular, that the selectivity in the formation of *p*-ethyltoluene in the alkylation of toluene with ethanol increases with increasing degree of saturation of HNaY zeolites with coke[240].

The research in this field is being continued. Hitherto, much art is still involved in dealing with the problem although the contribution of science has become incomparably greater.

VIII. THE STRUCTURE OF ZEOLITIC CATALYSTS, THE NATURE OF THE ACTIVE CENTRES, AND THE MECHANISMS OF THEIR ACTION

A characteristic feature of the development of catalysis in the presence of zeolites at the present stage is the increasing contribution of studies devoted to a more extensive investigation of the structure, the nature of the active centres, and the mechanism of the action of catalysts using a set of various physical, physicochemical, and theoretical (computational) methods. This is a natural result of the accumulation of extensive experimental data on the catalytic properties of zeolitic systems and the development of methods for the investigation of solids and chemical processes. Many new valuable results have been obtained in studies carried out in recent years. Data concerning the location of the exchangeable cations in zeolites of different compositions not only as regards crystallographic sites but also throughout the bulk of the crystals are of great interest. In particular, it has been established by X-ray photoelectron spectroscopy[216] that, in contrast to NaY and HNaY, for which no significant deviations of the surface Na^+ concentrations from those in the bulk phase are observed, the outer layers of the crystals of Na-mordenite and the TsVK and TsVM zeolites are greatly enriched in sodium. The migration of metals, produced on reduction of transition metal ions, to the outer surfaces of zeolite crystals[241] and the formation of alloys in polycationic systems when the latter are treated with hydrogen[241,242] have been demonstrated on many examples. It has been found that the oxidation of the Cu–Ni alloy in the CuNiY zeolite is accompanied not only by the formation of the CuO phase but also by the diffusion of the Cu^{2+} ions within the zeolite structure with appearance of isolated Cu^{2+} cations (as in the initial zeolite before reduction with hydrogen)[242].

Data concerning the influence of zeolites on the electronic state of deposited platinum and palladium have been surveyed[243] and valuable information has been obtained concerning the interaction of the metal with the aluminosilicate in other metal-zeolitic systems[244,245]. The characteristics of the spill over of hydrogen on zeolitic catalysts have been investigated[246]. Quantum-chemical calculations have been made for the OH groups[247,248] and also for the location of cations in faujasites[249]. An inhomogeneous distribution of aluminium in ZSM-5 type zeolites has been established. In their study of 50–200 μm single crystals by scanning electron microscopy and scanning X-ray microanalysis, von Ballmoos and Meier[250] found that aluminium is invariably concentrated at the edge of the crystals, while its content in the bulk of the particles is smaller by an order of magnitude than in the surface layers. The above differences depend on the size of the aluminosilicate crystals and the smaller the crystals the smaller the differences. According to Derouane et al.[251], the distribution of aluminium in the ZSM-5 zeolites depends also on the conditions of their preparation and even on the reactants used in their synthesis. These results lead to the conclusion that, in comparing the properties of zeolites with their composition determined by chemical analysis (the "average" composition), some caution must be exercised.

The above lists of examples is by no means complete and could be extended. The results obtained permit not only a more complete and accurate explanation of the characteristics of the action of catalysts but also promote the development of new approaches to the modification of catalysts and the solution of individual problems in the application of zeolitic systems. They also form part of the foundations of novel ideas concerning the mechanisms of certain reactions occurring on zeolitic catalysts[252].

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Such are the most important trends and the principal directions of development in catalysis on zeolites at the present stage. Zeolitic materials have aroused much promise for the solution of the important problem of the synthesis of artificial liquid and gaseous fuels and chemical products from coal and other mineral fuels. With their aid, much can be done not only in the field of the intensification of the processes and

the saving of energy and raw materials, but also in the solution of ecological and social problems.

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Catalysis in Polycondensation Reactions

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The importance of catalysis in polycondensation processes is considered. It is suggested that the catalytic processes in polycondensation reactions be divided into four groups: cationic, anionic, ionic-coordination, and free-radical. Examples of catalysts for a number of reactions are presented and the mechanisms of the catalytic action in various types of catalysis in polycondensation processes are considered. Such types of catalytic reactions are cationic and anionic catalysis and catalysis with the aid of tertiary amines, stereoregular polycondensation and polycondensation in the presence of catalysts of the Friedel-Crafts type, and oxidative polycondensation. The side reactions due to the presence of catalysts and their influence on the properties of the polymers obtained are examined.
The bibliography contains 60 references.

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I. INTRODUCTION

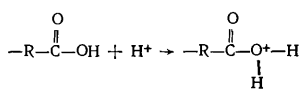
Since polycondensaton is an important method of synthesis of polymers, studies on polycondensation processes are vigorously developing at the present time. Many polymers obtained by polycondensation methods are nowadays manufactured in amounts running into millions of tonnes: these are phenol-formaldehyde and carbamide polymers as well as polyurethanes, polyamides, and polyesters[1,2]. Many polymers obtained by polycondensation are manufactured in amounts of thousands of tonnes: these include polycarbonates, unsaturated polyesters, polysiloxanes, polyoxides, and others. Finally the third group of numerous polycondensation polymers includes those whose manufacture is on a small scale but which are irreplaceable since they possess a set of valuable properties. These include thermostable polymers such as polyimides, polyarylates, polybenzimidazoles and other polyheteroarylenes, and also various semiconducting and light-sensitive polymers, etc. The great variety and wide range of properties of the polymers account for the vigorous development of studies on the polycondensation reaction, which is also reflected in the numerous articles, reviews, and monographs[1-10].

Catalysis plays a major role in polycondensation processes and the application of catalysts of all kinds is extremely widespread. The aim of the present review is to consider the literature data on catalysis in the polycondensation reaction[1,11,12].

II. TYPES OF POLYCONDENSATION PROCESSES

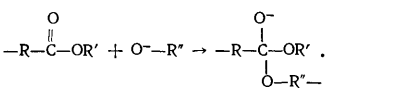
Depending on the nature of the catalyst and the starting materials employed, the polycondensation reaction can proceed as a cationic, anionic, polycoordination and even a free-radical process[3].

Thus the polycondensation of carboxylic acids with glycols in the presence of strong acids proceeds via a cationic mechanism with the intermediate formation of the product of the addition of a proton to the hydroxyl group of the acid:



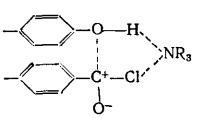
(1)

An example of anionic polycondensation is provided by the reaction of dicarboxylic acid esters with glycols in the presence of alkali metal glycolates, which proceeds in accordance with the equation



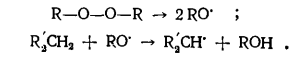
(2)

The polycondensation of dicarboxylic acid chlorides with bisphenols in the presence of catalysts such as tertiary amines is an example of the ionic-coordination polycondensation. This reaction leads to the formation of stereoregular polyarylates. Its mechanism can be accounted for by the formation of the following complex in its intermediate stage:



(3)

The formation of free radicals is an elementary step in the polyrecombination reaction [see reaction (4)], which is one of the instances of free-radical polycondensation[11]:



(4)

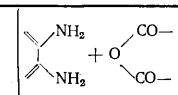
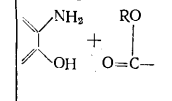
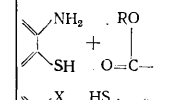
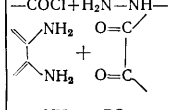
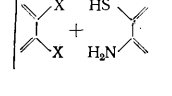
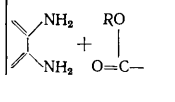
The examples presented illustrates the differences in the elementary step in polycondensation for each of the four types of polycondensation processes indicated above.

III. REACTIONS USED IN POLYCONDENSATION

An extremely significant feature of polycondensation processes, which has an appreciable influence on the process mechanism, is the great variety of types of initial monomers and hence differences between the structures of their active end groups whose reaction determines the course of the polycondensation process[1].

Table 1 lists the most important end groups and types of reactions used in polycondensation processes[12].

Table 1. The most important end groups and types of reactions used in polycondensation.

—COOH+HO—	>SiOH+HOAl<	—CO(CO)O+H₂N—	
—COOH+H₂N—	>BH+HB<	—RX+Na+XR—	
—COOR+HO—	>BH+HN<		
—COOR+H₂N—	=CH(OH)+M(OCOCR)₂*	—RX+Na₂S+XR—	
—COCl+HO—		—RX+H₂N—	
—COCl+H₂N—	—COCH₂X+H₂N—CS—	—ArH+HAr—	
—CONH₂+H₂N—	—COCl+H₂N—NH—	≡CH+HC≡	
>C=O+H₂N—		—ArH+XR—	
⩾CH+OC<		—Ar+O=C<	
—RX+M+XR—		—ArH+O₂+HAr—	
—ArX+M+XAr—		>SiOH+HOSi<	
—ArX+HO—			

*M = metal.

Table 2. The elements whose various compounds have been used as catalysts of the polyesterification reaction.

Periods	Groups							
	1	2	3	4	5	6	7	8
I	H	—	—	—	—	—	—	—
II	Li	Be	B	C	N	O	—	—
III	Na	Mg	Al	Si	P	S	Cl	—
IV	K	Ca	—	Ti	—	Cr	Mn	Fe, Co, Ni
	Cu	Zn	—	Ge	As	—	—	—
V	—	Sr	—	Zr	—	Mo	—	Pd
	Ag	Cd	—	Sn	Sb	—	—	Pt
VI	—	Ba	Ce	—	Ta	—	—	—
	—	Hg	—	Pb	Bi	—	—	—
VII	—	—	—	Th	—	U	—	—

IV. CATALYSTS FOR THE POLYCONDENSATION REACTION

Among the catalysts for the polycondensation reaction involving an ionic mechanism, one encounters a wide variety of compounds such as oxides, salts, inorganic and organic bases, alkalis, complexes, inorganic and organic acids, amines, etc[13–15]. As an illustration, Table 2 lists the elements whose various compounds have been used as catalysts in the polycondensation reaction[13,15–19].

It is noteworthy that the polyesterification reaction is a process for which catalytic problems have been studied in greater detail compared with other reactions. It was established that both the nature of the metal and the nature of the anion of the catalyst used play a significant role. Table 3 presents the catalysts employed in polyesterification processes.

Table 3. Polyesterification catalysts.

Catalyst		References
cation	anion	
H+	Cl⁻, $H_2PO_4^-$, HSO_4^-, $CH_3C_6H_4SO_3^-$, BO_3^{3-}, $C_6H_5COO^-$	[13, 16, 20, 21]
Li+, Na+, K+	Cl⁻, Br⁻, HSO_4^-, OH⁻, RO⁻, RCOO⁻, H⁻, SbO_4^{3-}	[16, 17, 22, 23]
Zn^{2+}, Mn^{2+}, Co^{2+}, Mg^{2+}, Cd^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Ti^{4+}, U^{6+}	RCOO⁻, Cl⁻, Br⁻, SO_4^{2-}	[15, 16, 17, 20, 24]
R_3N		[17, 25–28]
R_4N^+	OH⁻, Cl⁻	[17]
Pb^{2+}, Zr^{4+}, Al^{3+}, Ge^{4+}, Mg^{2+}, Ti^{4+}, Th^{4+}, Ta^{5+}, U^{6+}	O^{2-}	[16, 17, 22]
Ion-exchange resins		[29]

Table 4. Dependence of the rate constant k for the polycondensation of bis(β-hydroxyethyl) terephthalate on the nature of the catalyst.

Catalyst	$10^{-2}k$, g mmol^{-1}s^{-1}	Catalyst	$10^{-2}k$, g mmol^{-1}s^{-1}
GeO_2	326	$Co(Ac)_3$	61
$Sb(Ac)_3$	156	$Mn(Ac)_3$	32
$Al(Ac)_3$	131	Without catalyst	0.156

In order to characterise the dependence of the activity of the catalyst on its structure, we present as an illustration Table 4, which shows how the activity of the catalyst in the polyesterification reaction of bis(β-hydroxyethyl) terephthalate depends on the polarity of the metal ion[24]. The Table shows that the rate constant for this reaction increases sharply under the influence of the catalyst and there is a significant variation in the presence of different metals[24].

The activity of the catalyst in a specific process also depends on the nature of the reaction investigated. Thus in the synthesis of polyamides the activity of the catalyst is much lower than in the polyester synthesis. However, substances such as boric acid[30], zinc chloride[31], phosphoric acid[31], magnesium oxide[30], tetraethyl pyrophosphate[32], and other compounds[12] were nevertheless shown in many instances to be catalytically active in the synthesis of polyamides.

The polycondensation of α-aminoacid esters is known to be very sensitive to the action of catalysts[33]. Various acids, among which carbon dioxide is particularly active, are active catalysts for this reaction. The mechanism of the catalytic action of carbon dioxide on the polycondensation of α-aminoacid esters has been explained by the formation of *N*-carboxyaminoacid esters in the first stage, the esters subsequently giving rise to carbamates,

$$R'OOCCHRNH_3 \cdot HOOCNHCHRCOOR' , \qquad (5)$$

which decompose at 55 °C with formation of polypeptides[33].

A large group of polycondensation reactions includes the interactions of aldehydes with phenols, amides, and other derivatives. All these reactions are sensitive to the pH of

the medium and to the action of catalysts of different kinds. Table 5 lists the catalysts used in the reactions of phenols with aldehydes[11,34].

Table 5. Catalysts used in the reactions of phenols with aldehydes.

HCl	$CH_3C_6H_4SO_2NH_2$	$Zn(NO_3)_2$
H_2SO_4	$BeCl_2$	$Th(NO_3)_2$
H_3BO_3	$CuCl_2$	$UO_2(NO_3)_2$
$H_2C_2O_4$	$FeCl_3$	$Hg(NO_3)_2$
$HClO_4$	$SnCl_2$	$AgNO_3$
CCl_3COOH	$Ba(NO_3)_2$	NH_4NO_3
$(NaO)_2Zn$	$Al(NO_3)_3$	$NaNO_3$
$(NaO)_3Al$	$Mn(NO_3)_2$	KNO_3
NH_3	$Fe(NO_3)_3$	$Ca(NO_3)_2$
NaOH	$Ce(NO_3)_4$	$Mg(NO_3)_2$
KOH	$Ni(NO_3)_2$	$Co(NO_3)_3$
NR_3	$Cu(NO_3)_2$	$Cd(NO_3)_2$
$NH(CH_3)_2$	$Pb(NO_3)_2$	$Fe(SO_4)_2$
		I_2

In many polycondensation reactions alkylation or acylation takes place in the presence of Friedel-Crafts catalysts such as aluminium chloride, aluminium bromide, zirconium chloride, boron fluoride, and others[11,12].

The above examples of catalysts illustrate fairly clearly their great variety in different instances of polycondensation. As will be shown below, a common property of all the catalysts is their ability to form intermediates with reactants and hence to increase their chemical reactivity. It is also noteworthy that in many instances the initial monomers act as catalysts and the reaction can then be regarded as an example of self-catalysis.

V. THE MECHANISM OF THE ACTION OF CATALYSTS

The great variety of the structures and types of catalysts complicates the consideration of the mechanism of their action from a single standpoint. We shall therefore attempt to consider mechanisms common to each group of reactions.

In considering catalysis in polycondensation processes as a general phenomenon we must, on the one hand, deal with specific instances of catalysis in individual processes, and, on the other hand, an attempt must be made to survey its overall importance. The polycondensation process can be represented by the equation

$$x\,aAa + x\,bBb \rightarrow a\text{—}(\text{—}AB\text{—})_x\text{—}b + (2x-1)\,ab \quad . \qquad (6)$$

The role of catalysis can be represented in general form as a process involving the formation of an intermediate active compound of the catalyst (K) with one of the monomers via the mechanism

$$\begin{aligned} &a\text{—}A\text{—}a + K \rightarrow (a\text{—}A\text{—}a)\,K \quad ; \\ &b\text{—}B\text{—}b + K \rightarrow (b\text{—}B\text{—}b)\,K \quad , \end{aligned} \qquad (7)$$

followed by the reaction of the intermediate with a molecule of the second monomer;

$$\begin{aligned} &(a\text{—}A\text{—}a)\,K + b\text{—}B\text{—}b \rightarrow a\text{—}A\text{—}B\text{—}b + ab + K \quad ; \\ &a\text{—}A\text{—}a + (b\text{—}B\text{—}b)\,K \rightarrow a\text{—}A\text{—}B\text{—}b + ab + K \quad . \end{aligned} \qquad (8)$$

A version is also possible in which both monomers form compounds with the catalyst and subsequent reaction takes place between these two active intermediate molecules via the mechanism

$$(a\text{—}A\text{—}a)\,K + (b\text{—}B\text{—}b)\,K \rightarrow a\text{—}A\text{—}B\text{—}b + ab + 2K \quad . \qquad (9)$$

These considerations apply to the general character of the action of the catalyst. Considering the mechanism of the latter in greater detail, we shall attempt a more detailed consideration of the mechanism of the action of catalysts of different chemical types in a wide variety of polycondensation reactions. In view of the fact that all ionic polycondensation processes take place with formation of ions and ionic systems, all the catalysts of such reactions can be divided into three groups[11,12].

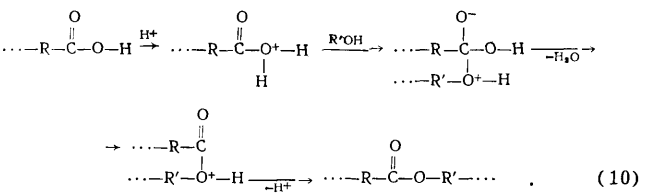
1. Catalysts which form reactive cations (cationic polycondensation).

2. Catalysts which form reactive anions (anionic polycondensation).

3. Catalysts which form reactive salt-like compounds (acceptor-catalytic polycondensation or stereospecific catalysis).

VI. CATIONIC CATALYSIS IN POLYCONDENSATION

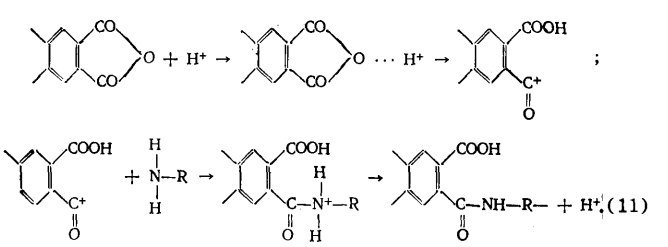
We shall now proceed to a more detailed consideration of the individual examples of the action of catalysts in each of the groups indicated above. In the equilibrium polycondensation of dicarboxylic acids and glycols in the presence of acid catalysts, the cationic reaction mechanism can be represented schematically as follows:



(10)

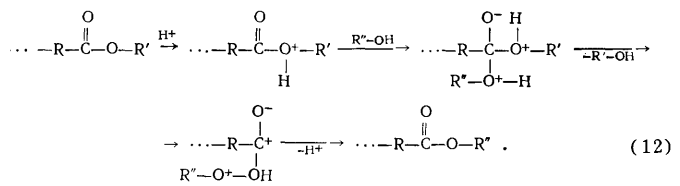
It is clearly seen from the above scheme that in the formation of oxonium compounds the addition of the acid proton to the hydroxyl group is an intermediate reaction in this process.

The carbonyl carbon atom becomes positively charged as a result and combines with the oxygen atom of the alcohol in consequence of nucleophilic attack. The reaction is accelerated in the presence of strong acids, since the initial glycol is a weak nucleophile and the initial dicarboxylic acid is a weak electrophile. However, the reaction can proceed via the above scheme also in the absence of a strong acid. Flory showed[35] that in this case the initial dicarboxylic acid plays the role of the catalyst. The catalytic action of carboxylic acids has also been demonstrated in the reactions of diamines and tetracarboxylic acid anhydrides, leading to the formation of polyamidoacids[36]. We believe that the reaction mechanism [see reaction (11)] can be represented schematically as follows:



(11)

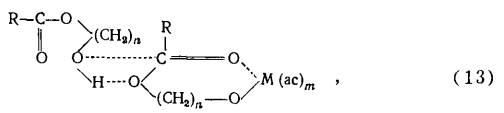
The mechanism of cationic polycondensation can be also illustrated in relation to the formation of a polyester via the transesterification of a dicarboxylic acid ester with a glycol in accordance with the equation



(12)

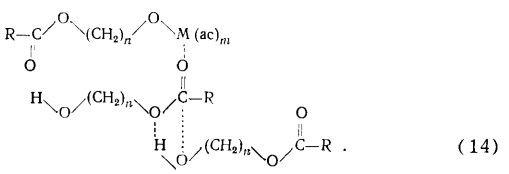
This reaction was investigated in particularly great detail in the synthesis of poly(ethylene terephthalate).[8,15,19,24,37,38]

Reinisch and coworkers[24] proposed the following mechanism of the action of catalysts in this reaction based on the formation of cyclic complexes:



(13)

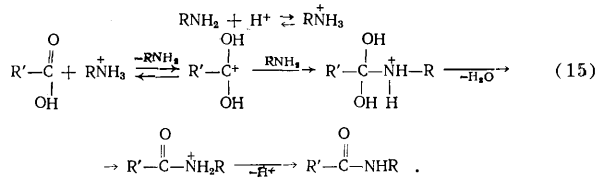
where M is a metal ion. There is a possibility of the simultaneous formation of linear complexes having the structure



(14)

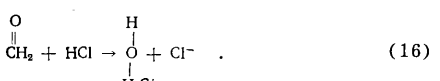
Here it is assumed that the activity of the catalyst is proportional to its ability to form complexes of this kind[24].

In the formation of polyamides the catalysis involves protons[39] [see reaction (15)]. The following mechanism, which explains the action of the acid, has been proposed:



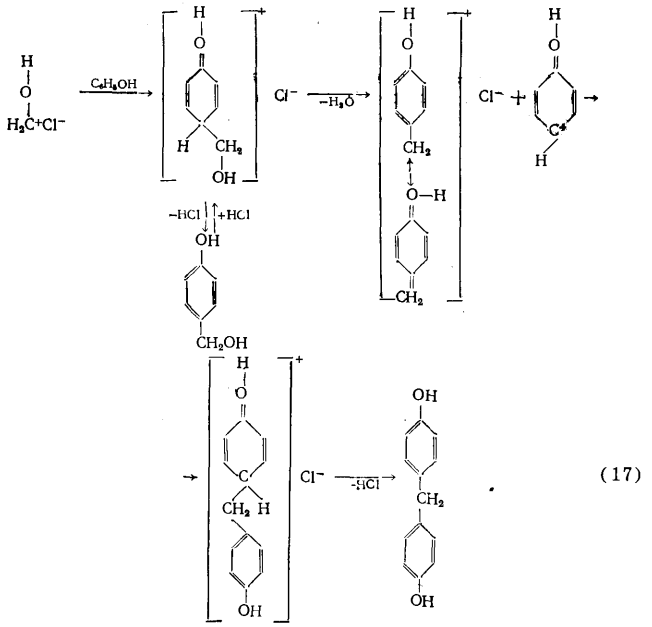
(15)

The reaction of phenols with aldehydes can proceed via a cationic mechanism in the presence of acids in accordance with the equation[40,41]



(16)

The ion pair formed in this process reacts further in the following manner:

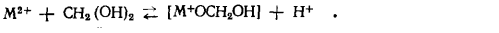


(17)

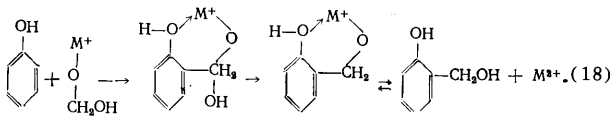
The first product is a quinone derivative, which is subsequently transformed into dihydroxydiphenylmethane. For this reason, phenol-alcohols are formed extremely rarely in an acid medium.

Bivalent metal ions accelerate the reaction of phenol with formaldehyde and at the same time exhibit a directing effect driving the hydroxymethyl groups in the *o*-positions relative to the hydroxy-groups. This results in the formation of phenolformaldehyde oligomers which contain predominantly *o*-substituted phenolic residues. These products are known as *ortho*-novolak or *ortho*-resol and are of interest as rapidly hardening materials.

Fraser et al.[42] described the catalytic action of bivalent metal ions in terms of the following scheme. The product of the reaction of the metal ion and methylene glycol is formed initially:

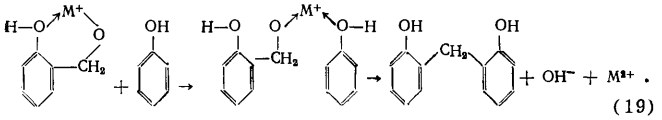


It then interacts with phenol to form *o*-salicyl alcohol



(18)

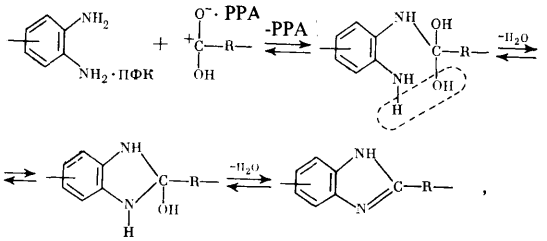
The last stage is the formation of di(*o*-hydroxyphenyl)methane:



(19)

The catalytic action of polyphosphoric acid has been explained by the formation of an intermediate complex in the synthesis of polybenzimidazoles in accordance with the

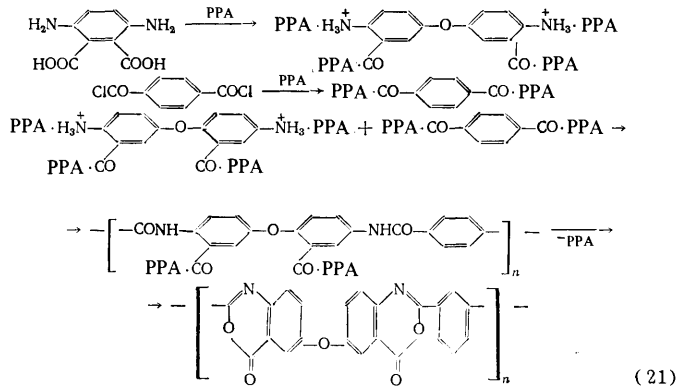
scheme[43]



(20)

where PPA is polyphosphoric acid.

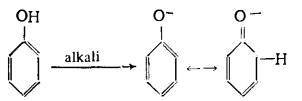
The formation of intermediate compounds with polyphosphoric acid has been demonstrated in relation to the formation of polybenzoxazinones from bisanthranilic acids[44]:



(21)

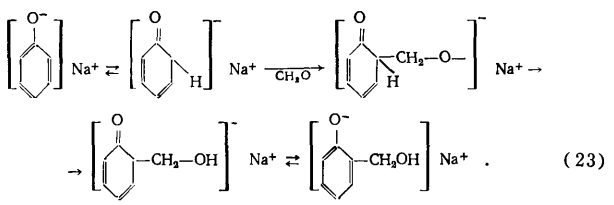
VII. ANIONIC CATALYSIS IN POLYCONDENSATION

The alkaline catalysts used in ionic polycondensation are extremely active, since in their presence phenol is converted into the phenoxide anion, which is accompanied by a redistribution of electron density in accordance with the following scheme:



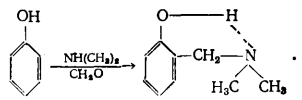
(22)

As a result of this, alkaline catalysts facilitate the reaction of phenols with aldehydes[40]. Accordingly, the action of an alkaline catalyst in the polycondensation of phenol with formaldehyde can be represented schematically as follows:



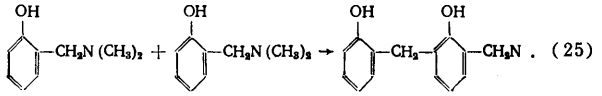
(23)

When dimethylamine is used, the reaction of phenol with formaldehyde proceeds with formation of an intermediate Mannich base[45] via the mechanism



(24)

The Mannich base thus produced decomposes on heating into dimethylamine and a phenol-formaldehyde polymer in accordance with the equation

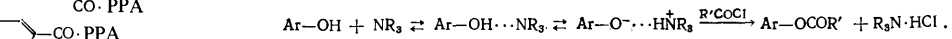


(25)

VIII. CATALYSIS WITH THE AID OF TERTIARY AMINES

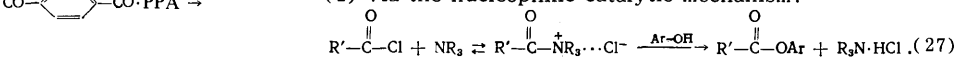
The acylation of alcohols and phenols by carboxylic acid chlorides in solution is frequently carried out in the presence of tertiary amines (pyridine, triethylamine, etc) as catalysts. Depending on the nature of the tertiary amine and the initial phenol and acid chloride, the reaction can then proceed via one of the following two mechanisms:

(1) Via the general base catalytic mechanism:



(26)

(2) Via the nucleophilic catalytic mechanism:



(27)

The result of the reaction of a dicarboxylic acid chloride with a bisphenol depends on the amount of catalyst—triethylamine. Fig. 1 illustrates the variation of the yield and molecular weight of the polyarylate obtained by the polycondensation of terephthalic acid dichloride (AC) in solution in dichloroethane with the amount of triethylamine (TEA).[46] The maximum in the plot of the viscosity against the amount of the catalyst is also observed for the reaction of dian with terephthalic acid chloride at a catalyst concentration of 20 wt.% (Fig. 2).[47]

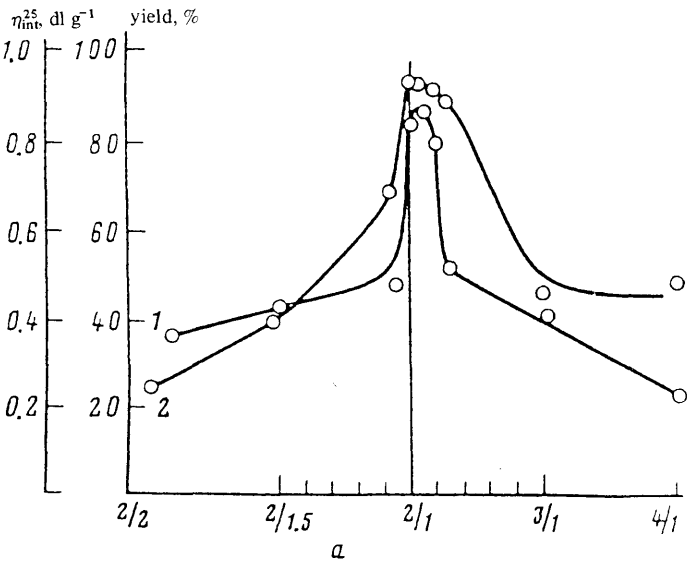


Figure 1. Dependence of the intrinsic viscosity (curve *1*) and the yield (curve 2) of the polyarylate on the molar ratio TEA:AC (*a*).

Tertiary amines not only accelerate the acylation reaction (for example, in the benzoylation of *p*-nitrophenol in the presence of triethylamine, the rate constant was higher by two orders of magnitude than for the same reaction in the presence of pyridine[48]) but also influence the steric structure of the polyester formed, as will be shown below[27,28,49].

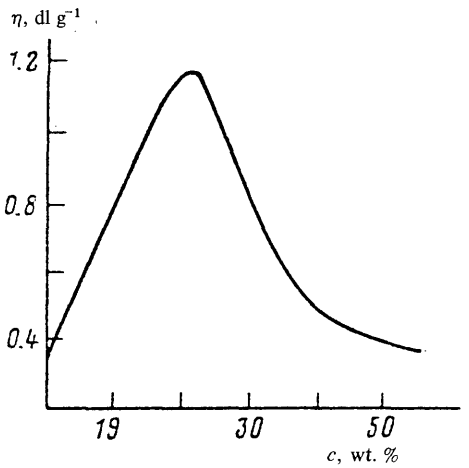


Figure 2. Dependence of the logarithmic viscosity of a solution of dian polyarylate and terephthalic acid on the amount of tetraethylammonium chloride (*c*) in the interfacial polycondensation reaction.

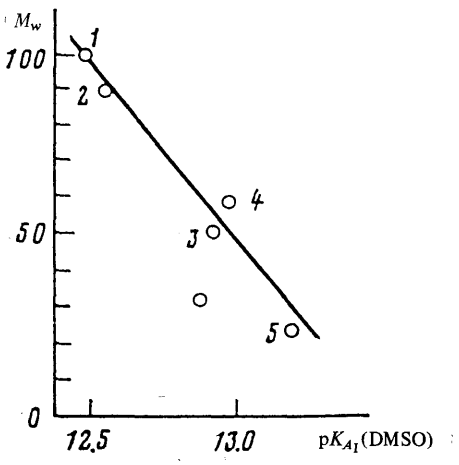


Figure 3. Dependence of the molecular weights of polyterephthalates M_W on the acidity of the bisphenol; bisphenol: *1*) 2,2-bis(3-chloro-4-hydroxyphenyl)propane; *2*) 3,3-bis-(4-hydroxyphenyl)phthalide; *3*) bis (4-hydroxyphenyl)methylphenylmethane; *4*) bis(4-hydroxyphenyl)phenylmethane; *5*) 9,9-bis(4-hydroxyphenyl)fluorene.

A characteristic feature of general base catalysis is also that, as can be seen from Fig.3, an increase of the acidity of the bisphenols entails an increase of the molecular weight of the polyarylates obtained from terephthalic acid chloride. Eqn.(26) shows that more favourable conditions for the acylation reaction are created with increase of the acidity of the phenol. Indeed an increase of the acidity of the hydroxy-component should entail an increase in its capacity for complex formation with the tertiary amine[48]. The increase of the activity of the hydroxy-component with increase of its acidity is indicated by the results of the joint acylation of a mixture of phenol and methanol with benzoyl chloride in the presence of triethylamine; it was found that the yield of phenyl benzoate was nine times greater than that of methyl benzoate. On the other hand, the reaction in the presence of a weak base such as pyridine led to the reverse ratio of the yields of phenyl and methyl benzoates, which was 0.35. This means that in the former case the general base catalysis predominates [reaction (26)], since the more acidic phenol is more reactive, whilst in the latter case nucleophilic catalysis predominates. This dependence of the rate of benzoylation of the mixture of the aliphatic alcohol and phenol on the basicity of the catalyst was confirmed by investigating the reactions using tertiary amines with different basicities as catalysts[49a]. It was found that the relative reactivity of the phenolic component increases with increasing basicity of the tertiary amine as can be seen from the curve in Fig.4.

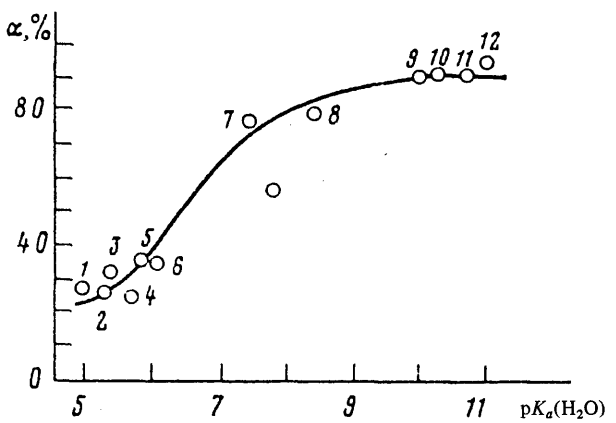


Figure 4. Dependence of the degree of conversion of phenol α on the basicity of the amine: *1*) quinoline; *2*) pyridine; *3*) isoquinoline; *4*) β-picoline; *5*) quinaldine; *6*) α-picoline; *7*) γ-collidine; *8*) triallylamine; *9*) ethyldimethylamine; *10*) cyclohexyldimethylamine; *11*) triethylamine; *12*) tributylamine.

These results confirm the above hypothesis that two catalytic processes can occur in acylation: general base catalysis and nucleophilic catalysis [reactions (26) and (27)].[49] The predominance of a particular catalytic process depends on the nature of the starting material and the tertiary amine[49]. The rate constants for the benzoylation of various phenols in the presence of triethylamine are presented in Fig.5. The left-hand part of the plot corresponds to phenols with pK_a ranging from 10 to 14. The sharp alteration in the form of the

plot starting from $pK_a > 14$ can be accounted for as a consequence of the change in the mechanism of the catalysis from the general base type to the nucleophilic type, as suggested above.

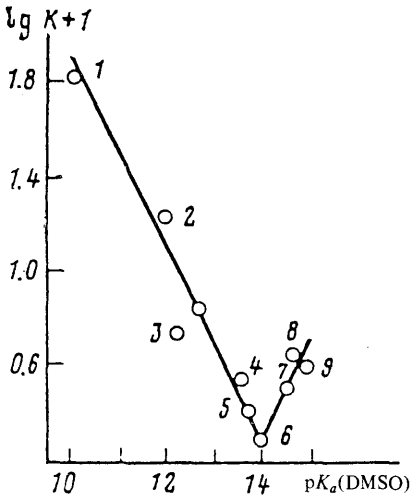


Figure 5. Dependence of the logarithms of the rate constants for the benzoylation of phenols on their acidity; phenol: *1*) *p*-nitrophenol; *2*) *p*-acetylphenol; *3*) *p*-chlorophenol; *4*) hydroquinone benzoate; *5*) phenol; *6*) *p*-t-butylphenol; *7*) *p*-cresol; *8*) *p*-methoxyphenol; *9*) hydroquinone.

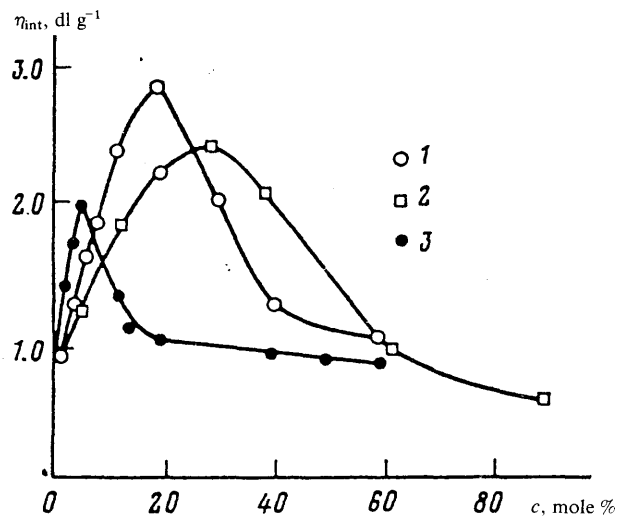
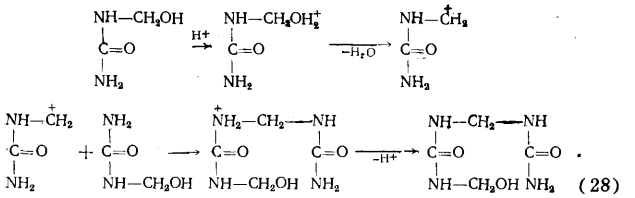


Figure 6. Dependence of the viscosity of the polyimide obtained by the reaction of the dianhydride of tricyclo [4.2.2.0]dec-10-ene-3, 4, 7, 8-tetracarboxylic acid with di(4-aminophenyl) ether on the catalyst concentration *c*: *1*) triethylamine; *2*) trimethylamine; *3*) tributylamine.[52]

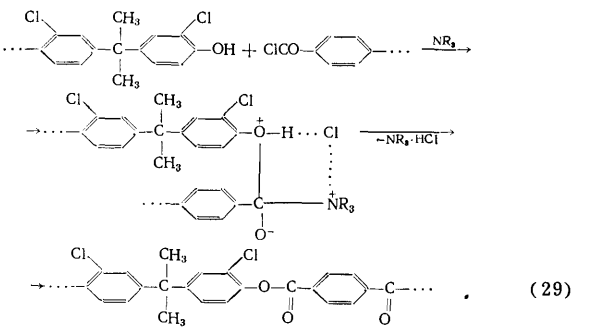
The reactions of diamines with dicarboxylic acid dianhydrides are extremely sensitive to the catalytic action of tertiary amines such as pyridine, triethylamine, and trimethylamine[50]. A maximum is then observed in the curves relating the viscosity of the product to the amount of the catalyst, as shown in Fig. 6.

The role of the acid catalyst in the reactions of amines and acid amides with aldehydes consists, according to Smets[51], in the formation of a carbonium ion in accordance with the equation

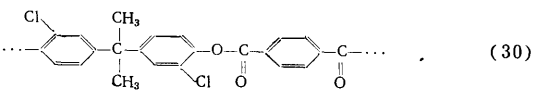


IX. CONFORMATIONALLY REGULAR POLYCONDENSATION

Stereoregular polycondensation was observed in the study of the polycondensation reaction in the presence of tertiary amines[27,28]. It proceeds as conformationally regular polycondensation on interaction of monomers capable of existing in several stereoisomeric forms [see reaction (29)]. The catalytic action of tertiary amines is manifested in the formation of polyarylates from bisphenols and dicarboxylic acid chlorides, which leads to the preferential formation of the *cis*- or *trans*-form of the polyester in accordance with the mechanism



In the presence of a weak base, for example, pyridine, the cisoid form of the polymer is formed. The use of a tertiary amine with strongly basic properties, for example, triethylamine, as the catalyst leads to the formation of the transoid form of the polyarylate:



The probable cause of the formation of conformationally regular polymers is the formation of stable conformations of the complexes of the starting materials with the tertiary amines.

X. POLYCONDENSATION IN THE PRESENCE OF FRIEDEL–CRAFTS CATALYSTS

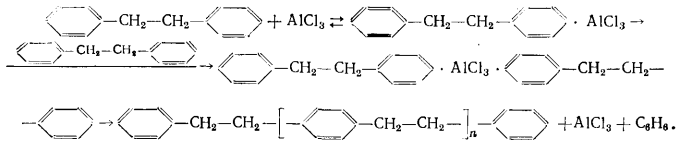
The polycondensation of aromatic hydrocarbons with halogen atoms in the side chain as well as the polycondensation of dihalogenoalkanes with aromatic hydrocarbons proceed only

in the presence of Friedel–Crafts catalysts. Aluminium chloride or the halides of cerium, boron, and other elements are most frequently used for this purpose.

A ternary complex of the halogenohydrocarbon with aluminium chloride and the aromatic hydrocarbon is formed as the first reaction product in this instance. The formation of such a complex in the polycondensation of dichloroethane with benzene can be described by the equation[53]:

$$ClCH_2CH_2Cl \cdot Al_2Cl_6 + 2C_6H_6 \rightleftarrows ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6 \qquad (31)$$

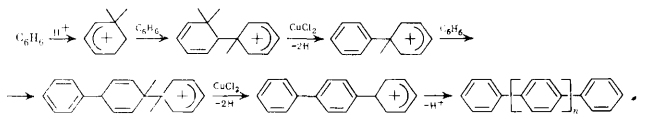
Catalysts act similarly in *trans*-arylation[54]. This type of polycondensation leads to the formation of polyarylenealkyls in the following reaction accompanied by the formation of benzene[54]:



(32)

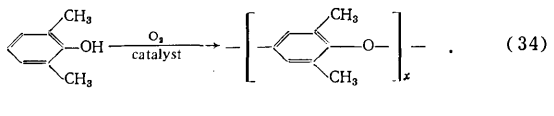
XI. OXIDATIVE POLYCONDENSATION

The oxidative polycondensation of benzene and other aromatic hydrocarbons, which leads to the formation of polyphenylenes according to Kovacic and Lange[55], takes place in the presence of iron(III) chloride or a mixture of copper(II) chloride and aluminium chloride[55]. The intermediate stage in this reaction is the formation of a σ-complex and the benzenium ion in accordance with the equation



(33)

An important instance of oxidative polycondensation is the synthesis of poly(2,6-dimethylphenylene oxide) by the oxidation of 2,6-dimethylphenol with atmospheric oxygen via the reaction



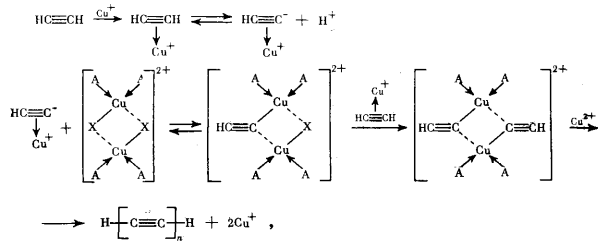
(34)

The reaction proceeds in the presence of various catalysts, among which the most important is the copper complex of pyridine[56]. The activity of this catalyst in the reaction depends on the ratio of the concentrations of pyridine and copper. With increase of this ratio, the number of ester linkages increases and the number of carbon–carbon bonds diminishes; when the ratio of the pyridine and copper concentration is 10:1, carbon–carbon bonds are not formed at all[57].

The copper complex of ammonia also proved to be an active catalyst of the oxidative polycondensation of acetylene, leading to the formation of a "carbyne"—a linear form of carbon—via the reaction[58]

$$HC \equiv CH \xrightarrow{+Cu^{2+}} -(-C \equiv C-)-_x \; . \qquad (35)$$

The mechanism of the action of the catalyst in this reaction can be described by the equation



where A = complexone residue.

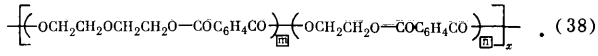
XII. SIDE REACTIONS INDUCED BY THE PRESENCE OF CATALYSTS

In considering the problem of the action of catalysts, one must bear in mind the fact that catalysts can influence not only the main reaction involving the synthesis of polymers but can also induce or accelerate various side reactions, which can involve both the initial monomers and the polymer formed and this can be reflected in the molecular weight and structure of the reaction product and can influence the entire set of its physical and chemical properties. In certain cases catalysts accelerate the decomposition of the polymer in the course of its synthesis, impairing its properties[16].

As an example of the negative influence of side reactions, one may quote the synthesis of poly(ethylene terephthalate) from ethylene glycol and terephthalic acid in the presence of sulphuric acid[11]. A side reaction involving the elimination of water and the formation of diethylene glycol then takes place:

$$2HOCH_2CH_2OH \rightarrow HOCH_2CH_2-O-CH_2CH_2OH + H_2O \; . \qquad (37)$$

In addition, acetaldehyde and ethylene acetal are also formed. The diethylene glycol produced reacts with terephthalic acid, which results in the formation of a hetero-unit polymer containing diethylene glycol units:



(38)

Acetaldehyde can be readily removed from the reaction mixture, which alters the ratio of the starting materials and has a negative effect on the molecular weight of the polymer.

The use of certain catalysts, such as, for example, titanium and aluminium compounds, leads to the formation of dark-coloured products[16]. The occurrence of such reactions necessitates caution in the selection of catalysts[15]. It has been noted that even the material of the reactor can influence the process and the polycondensation product[19].

In addition, one should point out that in certain cases the presence of the catalyst influences the mode of reaction. Thus Murochochi et al.[32] observed that *N*-(γ-aminobutyryl)-γ-aminobutyric acid gives rise to the cyclic γ-pyrrolidinone on heating. However, if this monomer is heated to 100 °C in diethylphosphinic acid in the presence of tetraethyl pyrophosphate, polybutanamide is formed.

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In conclusion of the review, we should like to emphasise that catalysis is a positive factor in polycondensation processes, since it accelerates the reaction, makes it possible to carry it out under mild conditions, and determines the microstructure of the polymer obtained. However, one should

note that theoretical studies of catalysis in polycondensation reactions fall short of the importance which they have for the development of this field. Therefore the problem of the selection of catalysts is still solved mainly empirically. The most important task for the future is the determination by extensive studies of the effective factors in the catalysis of polycondensation reactions, which should lead to the raising of the level of the relevant research and to advances in this field of polymer chemistry.

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